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Polytriazines

V.A.Pankratov and S.V.Vinogradova

The review deals with studies on the synthesis and properties of polymers containing the *s*-triazine ring in the main chain (polytriazine). These polymers have found large-scale application in many branches of engineering. Attention has been concentrated on studies dealing with the preparation of thermostable and heat resistant polymers based on *s*-triazine derivatives and also new and novel methods of synthesising these polymers, particularly such as the polycyclotrimerisation and polycyclocondensation reactions.

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I. INTRODUCTION

Polymers containing the cyclic *s*-triazine group in the main chain have been attracting attention for a long time. As early as in the 1930's a melamine-formaldehyde polymer was obtained by the polycondensation of melamine with formaldehyde[1] and subsequently found large-scale industrial application.

Recently there has been a considerable increase of interest in polymers containing *s*-triazine rings because the majority of polymers of this kind exhibit high thermal stability owing to the aromaticity of the *s*-triazine ring[2-4].

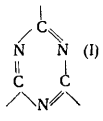
Polymers containing *s*-triazine rings may be obtained in two ways: (1) by the polycondensation or polymerisation of monomeric *s*-triazine derivatives and (2) by the polycyclotrimerisation of nitriles or by the polycyclocondensation of nitrile derivatives (iminoethers, amidines, etc.). Since the synthesis and properties of melamine-aldehyde polymers have been thoroughly reviewed[5-12], we shall not consider here (with some exceptions) studies dealing with triazine polymers of this type.

In the present review attention will be concentrated on problems of the thermal stability of polytriazines and also new, novel methods of their synthesis.

II. POLYTRIAZINES OBTAINED BY THE POLYCONDENSATION AND POLYMERISATION OF MONOMERIC *s*-TRIAZINE DERIVATIVES

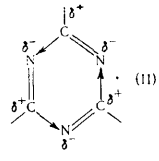
1. Polycondensation of Monomeric *s*-Triazine Derivatives

As mentioned above, *s*-triazine behaves like an aromatic compound[2-6]. It consists of a six-membered cyclic system of alternating N and C atoms:



(I)

which resembles the benzene cyclic system. The nitrogen atoms in *s*-triazine are more electronegative than the carbon atoms and the carbon–nitrogen bond tends to undergo type (II) polymerisation:



(II)

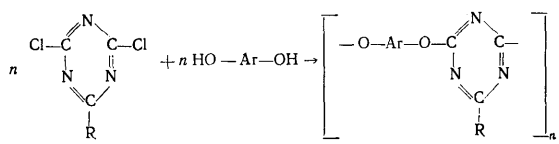
Apart from the χ-electron system, the *s*-triazine ring contains six unpaired electrons of the nitrogen atoms. Calculation of electron density in *s*-triazine[13] showed that it is 1.179 at a nitrogen atom and 0.821 at a carbon atom. This is probably the reason for the fundamental differences between the *s*-triazine and benzene systems: the *s*-triazine ring is less aromatic[14-16]. This is shown, in particular, by the lower chemical stability of the *s*-triazine system compared with the benzene ring.

Studies on *s*-triazine showed its inability to undergo electrophilic substitution reactions characteristic of benzene (nitration and sulphonation), so that it was impossible to synthesise nitro-derivatives of cyanuric chloride[2]. This can be explained only by the reduced electron density at the carbon atoms of *s*-triazine and the same explanation is also given for the greater mobility of the halogen atoms in its halogeno-derivatives, particularly of chlorine atoms in cyanuric chloride, which distinguishes the latter from benzene derivatives.

Cyanuric chloride and dichloro-*s*-triazines readily enter into substitution reactions with various compounds and therefore they constitute the main starting materials for the synthesis of polytriazines.

A number of polyesters—poly(aryl cyanurates)—with enhanced heat resistance and thermal stability have been

synthesised by the reaction of cyanuric chloride and dichloro-*s*-triazines with various bisphenols[17-35]:



Depending on the functional groups in the initial *s*-triazines, both linear soluble and cross-linked insoluble poly(aryl cyanurates) were obtained.

Thus Nakamura and coworkers[17] synthesised poly(aryl cyanurates) by the interfacial polycondensation of di-(4-hydroxyphenyl)propane with 2-R-4,6-dichloro-*s*-triazines, where R = OCH_3, $OCH_2CH{=}CH_2$, OC_6H_5, $N(C_2H_5)_2$, $N(CH_2CH{=}CH_2)_2$, $N(CH_2)_5$, $N(C_6H_5)_2$, C_6H_5, $PhNSO_2C_6H_4CH_3$, or Cl. Some of the poly(aryl cyanurates) obtained are crystalline and soluble in chloroform, *o*-dichlorobenzene, etc., films being formed from the solutions.

Cross-linked polymers[18-20], insoluble in the usual solvents but decomposing in hot alkalies and amines, have been synthesised by the interfacial polycondensation of cyanuric chloride with bisphenols [resorcinol, quinol, 4,4′-dihydroxybiphenyl, di-(4-hydroxyphenyl)methane, and di-(4-hydroxyphenyl)propane]. Vigorous thermal degradation of these polymers begins about 450°C.

Nakamura and coworkers[21,22] synthesised a number of poly(aryl cyanurates) using 2-diphenylamino-4,6-dichloro-*s*-triazine and various bisphenols and also a phenol-formaldehyde resin of the novolak type. The polymer based on di-(4-hydroxyphenyl)propane (dian) proved to have the highest molecular weight. It was found that the temperature of the onset of decomposition of the poly(aryl cyanurate) synthesised depends little on the type of the initial diol and is in the range 320–360°C (for an average molecular weight of about 5000). The majority of polymers dissolved in chloroform and nitrobenzene, but polymers based on quinol, 4,4′-dihydroxybiphenyl, di-(4-hydroxyphenyl)propane, and di-(4-hydroxyphenyl) sulphone were partly soluble only in nitrobenzene. Polymers with a fairly high molecular weight (in excess of 5000) are capable of forming colourless transparent films with high mechanical strength and a characteristic absorption in the ultraviolet.

Seta and Nakamura[23] obtained and successfully employed as dyes and stabilisers for various resins coloured poly(aryl cyanurates). Triazine dyes of this kind are synthesised by the polycondensation of diazo-derivatives of dichloro-*s*-triazine with bisphenols such as di-(4-hydroxyphenyl)propane, fluorescein, aurin, etc. The low-molecular polymers of different colours thus obtained (η_{inh} between 0.09 and 0.6 dl l^{-1}) proved to be readily soluble in chloroform, dimethylformamide (DMF), and dimethylacetamide.

In a later study Nakamura and coworkers[24] investigated the effect of the structure of poly(aryl cyanurates) on their thermal and mechanical properties. A large number of dichloro-*s*-triazines with 35 different substituents R in the ring were employed as the starting materials together with the following initial bisphenols: quinol, 4,4′-dihydroxybiphenyl, di-(4-hydroxyphenyl)methane, di-(4-hydroxyphenyl)propane, 4,4′-dihydroxybenzophenone, di-(4-hydroxyphenyl)sulphone, and phenolphthalein. The polymers obtained had high inherent viscosities (η_{inh} up to 3.52 dl g^{-1}) and their softening temperatures were in the range between 200° and more than 360°C. The authors established that the temperature of the onset of decomposition of these poly(aryl cyanurates) in air depends greatly on the structure of the substituents R in the triazine ring and is in the range 300–400°C. Poly(aryl cyanurates) with substituents such as $N(C_6H_5)_2$, $N\langle^{C_6H_5}_{(\beta\text{-naphthyl})}$, C_6H_5, etc. have the highest temperatures of the onset of decomposition. Poly(aryl cyanurates) based on phenolphthalein, 4,4′-dihydroxybenzophenone, and di-(4-hydroxyphenyl) sulphone are distinguished by high thermal stability.

Poly(aryl cyanurates) based on phenolphthalein and 2-diphenylamino-4,6-dichloro-*s*-triazine were described simultaneously by Devdariani and Kutepov[25], but they had less satisfactory thermal characteristics (softening temperature 160–210°C, temperature of the onset of decomposition 250–300°C) than those synthesised by Nakamura and coworkers[24], probably due to the lower molecular weights of the polymers synthesised (η_{inh} = 0.08–0.12 dl g^{-1}).

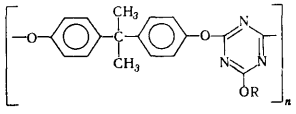
Vinogradova and Frenkel'[26] obtained poly(aryl cyanurates) by the high-temperature polycondensation in solution of 2-amino-4,6-dichloro-*s*-triazine with the anilide of phenolphthalein and 9,9-di-(4-hydroxyphenyl)fluorene in the presence of potassium or sodium carbonate. The polymer based on 9,9-di-(4-hydroxyphenyl)fluorene had η_{inh} = 0.18 dl g^{-1} in sulphuric acid and a softening temperature in excess of 320°C.

Later Anderbert and Neel[27] achieved under similar conditions the polycondensation of substituted dichloro-*s*-triazines $C_3N_3Cl_2R$ (R = NC_5H_{10}, C_6H_5, or OC_6H_5) with quinol, 4,4′-dihydroxybiphenyl, di-(4-hydroxyphenyl)sulphone, and di-(4-hydroxyphenyl)propane. The poly(aryl cyanurates) obtained had softening temperatures between 270° and 380°C and a temperature of the onset of decomposition (according to thermogravimetric data) in the range 305–415°C. These temperature characteristics of the polymers depend both on the structure of the substituent in the triazine ring and on the structure of the initial bisphenol. The poly(aryl cyanurates) based on 2,4-dichloro-6-phenoxy-*s*-triazine and quinol showed the highest thermal stability (380° and 415°C respectively)[27].

Korshak and Kutepov and coworkers carried out the high-temperature condensation of 2-anilino-4,6-dichloro-*s*-triazine with di-(4-hydroxyphenyl)propane and other bisphenols in solution[28-30] and in the melt[31], and established that, together with the main reaction, there is a homocondensation side reaction leading to the formation of three-dimensional products. When employed as hardening agents for epoxy-resins, the resulting oligomers and polymers increased the thermal stability of the resins[30,31].

Korshak, Kutepov, and coworkers[19,20,25,28-31] synthesised poly(aryl cyanurates), based on substituted dichloro-*s*-triazines [R = C_6H_5, $N(C_6H_5)_2$, $N(C_2H_5)_2$] and bisphenols such as 2,2-di-(4-hydroxyphenyl)propane, 2,2-di-(3-chloro-4-hydroxyphenyl)propane, 2,2-di-(2,5-dichloro-4-hydroxyphenyl)propane, and phenolphthalein as well as bisphenols containing various substituents at the central carbon atom, by high-temperature polycondensation in ditolylmethane in a stream of inert gas at 180–240°C. It was established that, depending on the structure of the substituents at the central carbon atom, the reactivity of bisphenols decreases in the series H, H > CH_3, C_6H_5 > H, C_6H_5 > C_6H_5, C_6H_5.

Breed and Elliott [32] synthesised two poly(aryl cyanurates) with the following structures by the polycondensation of substituted dichloro-*s*-triazines:

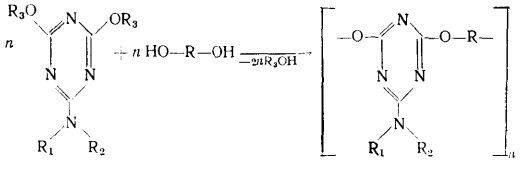


where R = $(CH_2)_4CH_3$ and $CH_2(CF_2)_4H$.

According to thermogravimetric analysis of polymers with similar inherent viscosities (0.89 and 1.24 dl g^{-1}), the polymer with the fluorinated substituent in the triazine ring has a higher thermal stability. Thus at 400°C the poly(aryl cyanurate) with R = $(CH_2)_4CH_3$ loses in air 19% of its weight (heating rate 6 deg min^{-1}) and 30% in an inert atmosphere (heating rate 3 deg min^{-1}), while the poly(aryl cyanurate) with R = $CH_2(CF_2)_4H$ loses only 3% of its weight in air and 3% in an inert atmosphere.

Anderbert and Neel [33,34] obtained linear polytriazines by the polycondensation in a high-boiling solvent at 200–240°C of substituted dichloro-*s*-triazines (R = NC_5H_{10}, C_6H_5, and OCH_3) with di-(4-hydroxyphenyl) sulphone, 2,2-di-(4-hydroxyphenyl)propane, 4,4′-dihydroxybiphenyl, and quinol. The resulting polymers were soluble in aniline, hexamethylphosphoramide, *N*-methylpyrrolidinone, etc. The polytriazines had a high softening temperature (270 and 585°C) and a temperature of the onset of decomposition in an inert atmosphere in the range 260–420°C.

Many polymers containing the *s*-triazine ring were obtained by the transesterification of dialkoxy-*s*-triazines with glycols [36]. The transesterification reactions proceed according to the mechanism



where R_1, R_2, and R_3 were varied from H to C_4H_9 and the glycols were ethylene glycol, di- and tri-ethylene glycols, hexa- and deca-methylene glycols, and also higher polyglycols with molecular weights up to 400.

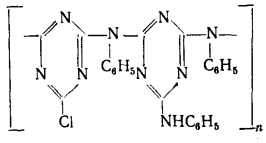
The degree of reaction was 85–90% and the polymerisation coefficient n = 4–5. The polymers were synthesised *in vacuo* at 80–160°C, the alcohol formed in the course of the reaction being distilled off. It has been noted that the transesterification reaction takes place in stages and at a high temperature infusible and insoluble polymers may be formed. Nakamura and coworkers [37–39] carried out the polycondensation of 2-R-4,6-diphenoxy-*s*-triazines, where R = OCH_3, OC_2H_5, $OCH_2CH{=}CH_2$, $N(C_2H_5)_2$, $N(CH_2CH{=}CH_2)_2$, $N(CH_2)_5$, $N(C_6H_5)_2$, *m*-$C_6H_3(CH_3)_2$, and Cl, with 2,2-di-(4-hydroxyphenyl)propane at 180–270°C in the presence of cadmium acetate. Low-molecular-weight linear polymers with a polymerisation coefficient of 3–10 were obtained. All the polymers, except that with R = Cl, were soluble in chloroform and dimethylformamide and had softening temperatures in the range 120–270°C. On further heating in the presence of dicumenyl peroxide, the polymers with R = $OCH_2CH{=}CH_2$ and $N(CH_2CH{=}CH_2)_2$ become cross-linked and insoluble.

Nakamura et al. [40] obtained linear polytriazines by heating (220–240°C) 2-amino-4-6-diphenoxy-*s*-triazine with 2,2-di-(4-hydroxyphenyl)propane *in vacuo*. It was established that in the first stage the reaction is of second order with an activation energy of 16.7–17.8 kcal $mole^{-1}$. Further heating of the polymer to 270°C without catalyst or in the presence of cadmium acetate leads to the formation of a cross-linked product, probably as a result of the elimination of phenol when phenoxy- and amino-groups interact. The authors [40] showed that the last reaction is identical with the homocondensation of 2-amino-4,6-diphenoxy-*s*-triazine on heating, since both processes are of second order and have similar activation energies (40.3–47.8 and 42.7 kcal $mole^{-1}$ respectively). The thermal stability of the cross-linked polymer thus obtained is somewhat higher than that of the product of the cross-linking of the linear polymer by paraformaldehyde, dimethyl terephthalate, tolylene di-isocyanate, etc.

Polyamides, polyimides, polyureas, and other classes of polymers obtained from triazine derivatives are distinguished by high thermal stability and heat resistance. Depending on the functional groups in these derivatives, polymers with both linear and three-dimensional structures can be obtained, as in the case of poly(aryl cyanurates).

One of the main starting materials for the synthesis of polymers of this type is cyanuric chloride and its various derivative, which Sheehan et al. [41] were the first to employ for this purpose.

Thus Ehlers and Powers [42] described the synthesis of thermostable polytriazyleneimides from cyanuric chloride and 2,4,6-triphenylamino-*s*-triazine, whose structure may be represented by the following formula:

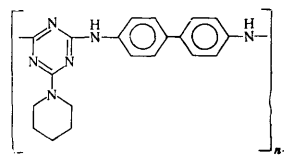


Thermostable and chemically stable polymers have been obtained by the polycondensation of cyanuric chloride or dichloro-*s*-triazines with various aromatic diamines [19,20,26,27,42–46].

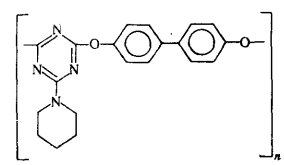
Triazine-containing polymers based on 2-amino-4,6-dichloro-*s*-triazine and hexamethylenediamine, *p*-phenylenediamine, and anilinephthalein have been described [26]. The polycondensation was carried out in a stream of nitrogen in n-butyl alcohol in the presence of triethylamine (12 h with a gradual increase of temperature from 85° to 115°C) or in decalin in the presence of sodium carbonate (at the boiling point of the solvent for 18 h). The polymers of hexamethylenediamine and *p*-phenylenediamine, synthesised in n-butyl alcohol, had inherent viscosities of 0.13 dl g^{-1} (in dimethyl sulphoxide) and 0.14 dl g^{-1} (in sulphuric acid) respectively. Their softening temperatures were 290–320°C and about 450°C respectively. The polymer based on anilinephthalein had a softening temperature of 260–270°C and was more soluble than the above polymers (it was soluble in dimethyl sulphoxide, dimethyl formamide, and dioxan). The polyamide based on hexamethylenediamine and synthesised in decalin was infusible and insoluble.

Andebert and Neel [27] carried out the high-temperature polycondensation of various dichloro-*s*-triazines with diamine derivatives or related compounds such as piperazine hydrochloride, benzidine, 2,4-diamino-6-phenyl-*s*-triazine, and hexamethylenediamine in decalin. It is noteworthy that the polyamides greatly surpass (by 100–150°C) in both heat resistance at thermal stability the poly(aryl cyanurates) with comparable structures obtained

in the same study[27]. Thus the polyamide based on benzidine,



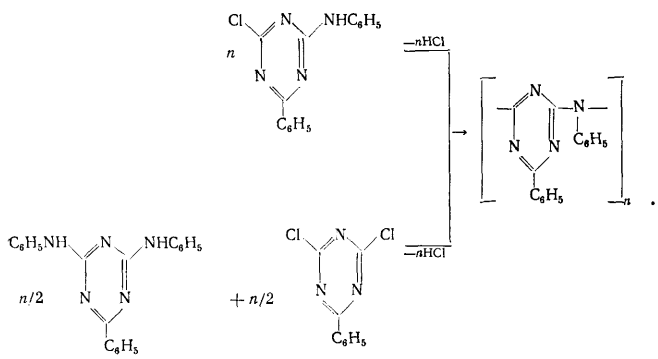
has a softening temperature at 470°C and begins to decompose *in vacuo* at 460°C (η_{inh} = 0.32 dl g^{-1}), while the corresponding temperatures for the poly(aryl cyanurate) having a similar structure and based on 4,4′-dihydroxybiphenyl,



are 315–320° and 365° respectively (η_{inh} = 0.23 dl g^{-1}).

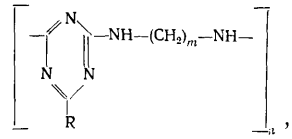
Polycondensation of 2,4-diphenoxy-6-chloro-*s*-triazine with di-(4-aminophenyl) sulphone yielded a polymer melting at 360°C and stable on heating in air to 400°C.[43] Among polymers of this type, polyperfluoro-4,4′-diphenylmelamine proved to be the most thermostable[44]. It is stable up to 500°C but at 700°C in air it loses 63% of its initial weight.

Ehlers and Ray[45] established that it is more convenient to employ chloro-derivatives of *s*-triazine rather than phenoxy-derivatives in the polycondensation with the aim of obtaining linear polytriazyleneimides:



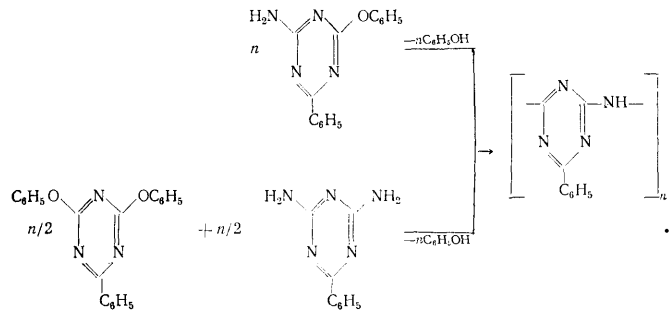
They also established that the polycondensation is best performed in an inert atmosphere at 200–250°C without reducing the pressure; the latter condition is necessary owing to the ease of sublimation of the initial monomers at a high temperature (about 200°C), while at a 150°C the reaction hardly occurs. It was shown that acids, alkalies, peroxides, and HCl acceptors do not affect the molecular weight of the polymer formed. It is noteworthy that the polymers containing terminal and side chain chlorine atoms are hydrolysed in air, becoming brittle and insoluble. Attempts have been made to replace these chlorine atoms by phenoxy-groups by treating the polymer with phenol, but the polymer decomposed under these conditions.

Infusible and insoluble polymers thermostable up to 400°C are formed in the high-temperature homocondensation of a number of amino-derivatives of *s*-triazine[45]. The most thermostable of these proved to be the polymer obtained from 6-anilino-4-chloro-2-phenyl-*s*-triazine. It loses 5% of its weight at 400°C and not more than 25% at 900°C. Polymers containing guanamine units separated by aliphatic bridges were obtained by the polycondensation of cyanuric chloride or its derivatives with aliphatic diamines:



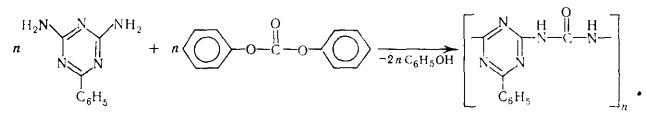
where R = Cl, C_6H_5, a monoamine residue, etc. and m = 6–12.[26,27,47]

Linear soluble polyamides containing *s*-triazine rings were obtained by the homocondensation of 4-amino-6-phenoxy-2-phenyl-*s*-triazine or by the reaction of 4,6-diphenoxy-2-phenyl-*s*-triazine with guanamines[48,49]:



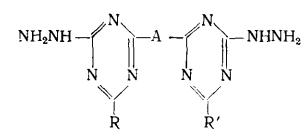
The transamination reaction was performed in an atmosphere of nitrogen above the melting point of the monomers; the optimum reaction temperature is 260–300°C. Polymers with maximum molecular weights (according to viscometric data) are obtained when the synthesis is carried out at a reduced pressure. The homopolymer of 4-amino-6-phenoxy-2-phenyl-*s*-triazine and a polymer based on 4,6-diphenoxy-2-phenyl-*s*-triazine and benzoguanamine have the same physical properties, which is evidence of the identity of their structures. This is also confirmed by infrared spectroscopic data.

The polymer obtained by the polycondensation of 2,4-diamino-6-phenyl-*s*-triazine with diphenyl carbonate exhibits a high heat resistance[48]:



It is soluble in sulphuric acid and melts at 350°C.

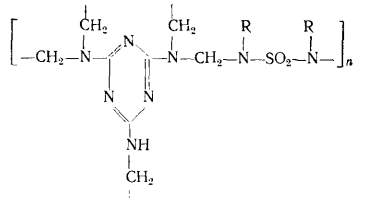
Insoluble polymers are formed in the homopolycondensation of 2,4-diamino-6-phenoxy-*s*-triazine and 2-amino-4,6-diphenoxy-*s*-triazine[50,51]. Gehm et al.[52] obtained film-forming polymers with viscoelastic properties by the interaction of linear polyhydroxy-compounds, modified using isocyanate (M = 750–6000), with compounds of the type:



where R and R′ = H, Cl, alkyl, aryl, etc. and A is a bivalent diamino-residue linked via N atoms to the *s*-triazine rings, for example a diamino-residue with 2–12 carbon atoms in the chain.

Polymers with high thermal stability and resistance to oxidation were obtained by heating a mixture of dihalogeno-derivatives of aromatic compounds (for example *p*-dichlorobenzene) and 2,4,6-tri-(*p*-chlorophenyl)-*s*-triazine with sulphur in the presence of alkali or alkaline earth metal carbonates, sulphides, and oxides[53]. The decrease of the weight of the resulting polymers was 3.3% after heating for 100 h at 300°C and 5.3% after 20 h at 400°C.

Polymers with the following structure were obtained by the polycondensation of formaldehyde with sulphamide or its mono- and di-alkyl-substituted derivatives (RNH–SO_2–NH–R) and melamine[54,55]:



where R = CH_3, t-C_4H_9, etc. These polymers lose 25% of their weight at temperatures up to 225°C; the N–H and N–SO_2 bonds in the polymers persist up to 225°C; the *s*-triazine ring does not break down up to 300°C.[54]

Kabaivanov and Alaminov achieved the synthesis of low-molecular-weight thermoplastic resins by the polycondensation of phenol, formaldehyde, and cyanuric acid in the presence of both acid[56] and alkaline[57] catalysts. They established that the reaction proceeds via the formation of hydroxymethyl derivatives of cyanuric acid. Articles made from the resulting Resol resins are distinguished by high thermal stability, water resistance, good mechanical strength, and incombustibility.

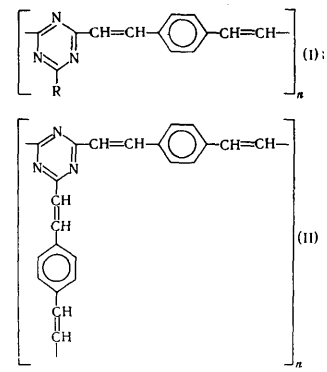
The same authors[58,59] obtained resins based on cyanuric acid, 2,2-di-(4-hydroxyphenyl)propane, and formaldehyde. The polymers were synthesised in an acid medium with different proportions of the initial components. The polycondensation reaction was investigated spectroscopically. It was shown that cyanuric acid reacts in the keto-form; at 130°C methyl ether groups are formed predominantly, rearranging at a higher temperature (170°C) to methylene bridges with liberation of formaldehyde[60].

A characteristic feature of the majority of the polytriazines discussed above is the presence in the macromolecular chain of heteroatoms (O and N) linking the *s*-triazine rings either directly with one another or via another group.

Next we shall consider studies on the synthesis and properties of polytriazines in which the *s*-triazine rings are linked via hydrocarbon groups.

Greth and coworkers[61,62] described the synthesis of polymers with a system of conjugated double bonds containing *s*-triazine rings in the chain and investigated some of their properties. The authors undertook the synthesis of these polymers on the basis of the fact that the *s*-triazine ring is an aromatic system with a high resonance energy and therefore polytriazines should have a high thermal stability.

Polycondensation of 2,4-dimethyl-6-phenyl-*s*-triazine, 2-methoxy-4,6-dimethyl-*s*-triazine, and 2,4,6-trimethyl-*s*-triazine with terephthalic dialdehyde yielded linear (I) or cross-linked (II) conjugated polytriazines[61,62]:

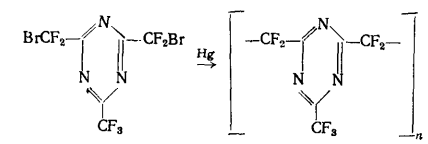


where R = C_6H_5 or OCH_3. Polymers of type (I) begin to decompose in a stream of nitrogen at 380°C (4% weight loss) and decompose vigorously at 530°C; at 730°C they lose 40% of their weight. In oxygen the polymer loses at 380°C only 4% of its weight but at 700°C its combustion is complete.

A polytriazine of type (II) loses 8% of its weight at 500°C in a stream of nitrogen, 30% at 700°C, and 40% at 875°C. The degradation of this polymer in a stream of oxygen begins, like that of polymer (I), at 380°C and at about 600°C its combustion is complete[63].

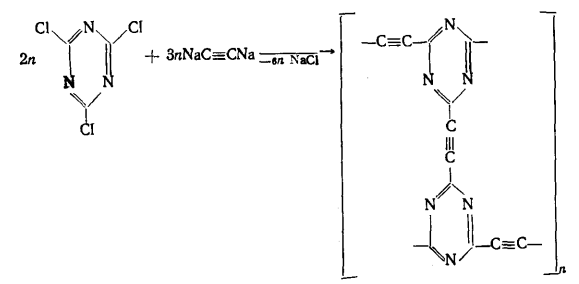
Nitriles, which are usually formed in the depolymerisation of low-molecular-weight triazines, were not detected in the degradation products of polytriazines[63].

Linear polyperfluoroalkylenetriazine polymers, which are of considerable interest as high-temperature elastomers (temperature at the onset of decomposition about 400°C, see below—pp. 72–74), were synthesised by the polycondensation of difunctional fluorinated triazine monomers containing an active halogen[64] at 250–300°C in the presence of metallic mercury. The reaction of 2,4-di(bromodifluoromethyl)-6-trifluoromethyl-*s*-triazine takes place according to the mechanism:



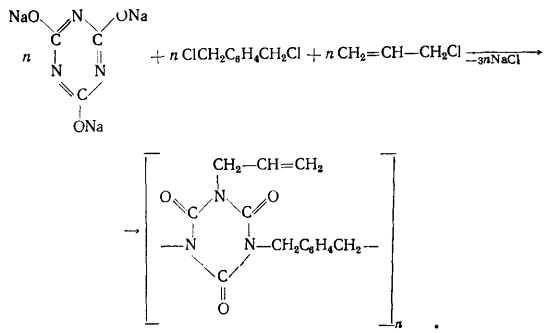
Above 40°C the resulting polymer exhibits rubber-like properties.

Paushkin et al.[65] obtained polymers by the polycondensation of cyanuric chloride with sodium carbide by the reaction



The infrared spectrum of the polymer has absorption bands in the region of 1540 and 1570 cm^{-1} which in all probability characterise the triazine rings in the polymer.

Fusible and soluble polymers with a softening temperature of about 200°C and containing isocyanurate rings in the chain were synthesised by the joint polycondensation of allyl chloride and *p*-xylylene dichloride with sodium cyanurate[66]:



2. Polymerisation of Monomers Containing the *s*-Triazine Ring

As already mentioned at the beginning of the review, one of the common methods for the introduction of the *s*-triazine ring into the polymer chain is by polymerising monomeric *s*-triazine derivatives. Depending on the functional groups in the unsaturated triazine derivatives, both linear and three-dimensional polymers may be obtained.

Data have been published both on the homopolymers of unsaturated *s*-triazine derivatives[67-76] and on their copolymers with other unsaturated compounds[68,71-73,76-90]. *s*-Triazine derivatives are as a rule introduced into copolymers to improve their thermal stability. Moreover, the presence of a large number of unsaturated functional groups in the triazine ring promotes the formation of a large number of cross-links, which also lowers the rate of thermal degradation of highly-structured polymers based on them.

One of the most widely used unsaturated monomers containing the *s*-triazine ring is triallyl cyanurate[77-88,91]. It is readily miscible with unsaturated polyesters and therefore has come to be widely used as a modifying and structure-forming agent in alkyd resins[77-85].

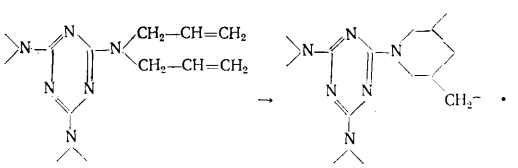
According to the data of Cohen and Cypher[86], who investigated the copolymers of poly(ethylene glycol maleate) and poly(diethylene glycol maleate) with diallyl phthalate, isophthalate, and terephthalate and with triallyl cyanurate, the thermal stability of the copolymers varies in the following sequence as a function of the monomer employed in the copolymerisation: triallyl cyanurate > diallyl terephthalate > diallyl isophthalate > diallyl phthalate. The high thermal stability of copolymers with triallyl cyanurate is due, according to the authors, to the thermal stability of the *s*-triazine ring in the initial monomer. In the same study[86] it was shown that the replacement of the allyl group in triallyl cyanurate by the ethoxy-group does not alter the thermal stability of the polymer: the methyl group decreases and the β-hydroxyethyl group sharply increases the thermal stability of the polymer. This finding was explained by the increase in the number of substituents in the monomer as a result of the side reaction involving the formation of dimeric cyanurate. Another explanation may be the involvement of the hydroxyethyl group of the monomer in the cross-linking of the polyester.

There are data on the use of triallyl cyanurate also for other purposes, for example for the preparation of transparent materials used to make lenses and other articles[87]. The products of the transesterification of triallyl cyanurate with glycols are used as plasticisers for a number of resins[87,88]. Oswald[91] stabilised halogen-containing polyolefins with cyanurates or isocyanurates. It was found that chlorinated polyethylene stabilised with 0.5–10% of triallyl cyanurate does not change over a period of 1 h at 200°C.

Linear triazine polyesters with allyl groups in the side chain were obtained by the transesterification of triallyl cyanurate with glycols in the presence of sodium methoxide as a catalyst[88]. Linear unsaturated triazine polyesters were synthesised only in the very initial stage of the reaction; when the degree of reaction is more than 0.15, polymers with three-dimensional structures are formed exclusively.

The synthesis of unsaturated polyesters by the copolymerisation of alkenyl alkyl esters of cyanuric acid with unsaturated aliphatic and alicyclic hydrocarbons in the presence of radical polymerisation initiators has been reported[79,88].

Gillham and Petropolous[67] investigated hexa-allylmelamine polymers. Piperidine rings alternating with *s*-triazine rings may be formed in the radical polymerisation of hexa-allylmelamine by the reaction



Owing to the high degree of cross-linking, these polymers have good mechanical properties and a high thermal stability. The polymers are stable up to 370°C on heating in air and up to 400°C on heating in nitrogen. Their thermal stability is higher than that of polymers based on triallyl cyanurate. Transparent plastics based on hexa-allylmelamine are stable in air up to 260°C

Oligomeric unsaturated polyesters based on hexa(hydroxymethyl)melamine, partly esterified with allyl alcohol and maleic acid, have been described[92].

There are also literature data on the modification of unsaturated polyesters by compounds based on *s*-triazine. Thus the use of cyanuric acid and its derivatives as modifying components has been described[93].

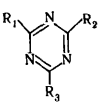
Widmer[89] described the synthesis and structure of new resins suitable for the preparation of varnishes, based on the allyl ether of hydroxymethylmelamine and its copolymers with vinyl monomers. The varnishes obtained from these resins dry rapidly and the coatings are distinguished by high hardness and resistance to solvents.

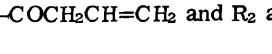
Kugel and coworkers[68] achieved the synthesis of 2,4-dimethyl-6-vinyl-*s*-triazine by the pyrolysis of the corresponding acetoxyethyldimethyl-*s*-triazine, polymerised it, and investigated the properties of the polymer. They found that the initial monomer polymerises at 20°C under the influence of free-radical initiators (benzoyl peroxide, etc.) or radiation, and readily copolymerises with styrene, methyl methacrylate, and acrylonitrile. The kinetics of its copolymerisation with styrene and methyl methacrylate have been investigated. The homopolymer softens at 105°C and readily dissolves in water and the usual organic solvents, with the exception of aliphatic hydrocarbons.

Pyrolysis of the corresponding acetoxyethyl- or acetoxyisopropyl-*s*-triazine also yielded 2,4-diethyl-6-isopropenyl-6-methyl-2,4-divinyl-, 2-butyl-4,6-divinyl-, 2,4,6-trivinyl-, 2,4-di(trichloromethyl)-6-vinyl-, 2,4-di(pentabromoethyl)-6-vinyl-, and 2,4-di(pentafluoroethyl)-6-isopropenyl-*s*-triazines[76]. They have been homopolymerised and copolymerised with alkyl acrylates, styrene, vinyltoluene, and other monomers in the presence of radical initiators. These homopolymers may be used in the manufacture of thermostable sheets and fibres.

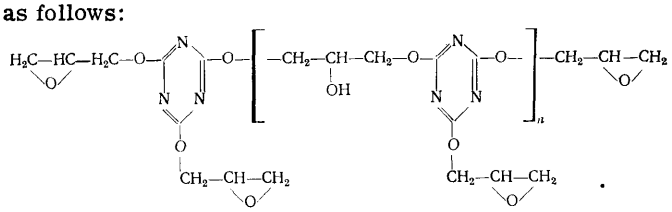
Vinyl derivatives of guanamines—2,4-diamino-6-(α-vinyloxyalkyl)-*s*-triazines[69] and acylamino-*N*-(vinyloxyalkyl)guanamines[70]—are polymerised in the presence of strong acids (H_3PO_4) or are used for polycondensation with formaldehyde. The copolymerisation of hexahydro-1,3,5-triacryloyl-*s*-triazine with styrene, vinyl acetate, methyl methacrylate, and acrylonitrile has been investigated[90]. There are various patent data on the vinyl esters, amides, and other derivatives of *s*-triazine[71-73] which form homopolymers and copolymers with vinyl monomers.

Holtschmidt[75] obtained polytriazines with a high thermal stability by radical polymerisation of compounds of the type



where R_1 =  and R_2 and R_3 = R_1, H, halogen, etc.

Poly(glycidyl cyanurates)[94-99], obtained by the reaction of cyanuric acid with epichlorohydrin or of cyanuric chloride with 2-hydroxymethyloxiran, have been described[94-99]. The initial product was triglycidyl cyanurate, which subsequently forms poly(glycidyl cyanurate) resins. The general structure of such resins can be represented as follows:



(where n = 0 - 2).

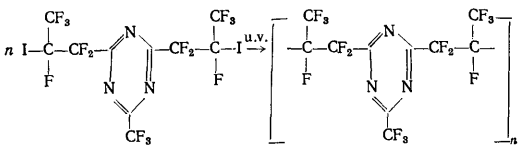
Usually poly(glycidyl cyanurate) resins contain between 0.8 and 10% of chlorine, which is evidence of an incomplete conversion of the chlorohydrin groups. In order to reduce the chlorine content, the resin is subjected to additional dehydrochlorination with a solution of alkali, which makes it possible to increase the number of epoxy-groups. Poly(glycidyl cyanurate) resins, hardened with the usual hardening agents employed for epoxy-resins, have a higher thermal stability and lower dielectric losses at high temperatures than ED-6 epoxy-resin.

Apart from the polymers of triglycidyl cyanurate, the polymers of other epoxy-derivatives of *s*-triazine have been described[100-104].

Three-dimensional polymers insoluble in organic solvents are obtained by heating a mixture of cyanuric acid with the di-isocyanate esters $R(NCO)_2$, $R-PO-(NCO)_2$, or $R-P(NCO)_2$, where R is an aliphatic or aromatic group. The reaction is carried out in the presence of an excess of cyanuric acid. The polymers are stable up to temperatures in excess of 300°C.[105]

Nakamura and coworkers[37-39] described a method for the preparation of novolaks containing *s*-triazine rings with unsaturated side groups: 2,4-diallylamino-6-chloro-*s*-triazine was allowed to react with phenol, t-butylphenol, and novolak. Polycondensation in the presence of alkali at 100–105°C yielded unsaturated products with different molecular weights and different numbers of functional groups. Such polymers may be hardened with radical-polymerisation initiators or may be structured with methyl methacrylate and styrene.

Griffin[64] investigated the possibility of using the polyrecombination reaction for the synthesis of polyfluoroalkyltriazine polymers. In particular, these polymers are formed by the following mechanism when di(iodoperfluoroalkyl)-*s*-triazines are exposed to ultraviolet light:



Thermostable elastomers were obtained in this way. However, owing to the high cost of the monomers, this method of preparing fluorinated triazine elastomers cannot as yet compete with other syntheses of these polymers (see below—pp. 72–74).

III. POLYTRIAZINES OBTAINED BY POLYCYCLOCONDENSATION AND POLYCYCLOTRIMERISATION REACTIONS

In contrast to the methods of preparation of polytriazines described above, where the *s*-triazine ring was introduced with the initial monomers, this section deals with the formation of the *s*-triazine ring in the course of the synthesis of the polymer. Since in this case polytriazines (and also other polymers) may be formed by polycondensation or polymerisation reactions in which three functional groups of the initial monomers must be involved at once, these reactions have been called, following the suggestion of V. V. Korshak, polycycloconden-sation and polycyclotrimerisation respectively.

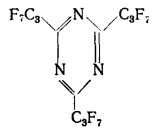
The synthesis of polytriazines (as well as other polymers) by these two methods has been widely used only in recent years. However, the high promise of these syntheses is already evident.

The advantages of the synthesis of polymers by polycondensation and particularly by polycyclotrimerisation include the possibility of the specific synthesis of both highly structured polymers, the rings of which are separated by various bridging groups, and linear polymers. The polycondensation or polymerisation may be interrupted at the oligomer stage, the oligomers being processed by the usual methods.

1. Polycyclocondensation of Nitrile Derivatives

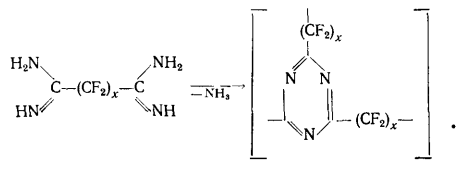
As already stated above, the polycyclocondensation reaction has only comparatively recently come to be widely employed for the synthesis of polytriazine polymers. This method of polycondensation became particularly interesting in connection with Brown's discovery of the class of polyperfluoroalkylenetriazine elastomers with high thermal stability and physicomechanical parameters[106-108].

Fluorocarbon elastomers are known to be stable for a long time at temperatures not exceeding 300°C. At the same time the exceptionally high resistance of perfluoroalkyltriazines with the structure[109]

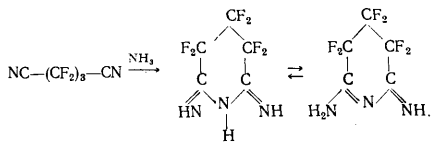


to thermal oxidation suggested that the problem of increasing the thermal stability of fluoro-polymers may be solved by introducing *s*-triazine rings into their structure. Perfluoroalkylenetriazine polymers, which combine a high thermal stability (about 400°C), exceeding the thermal stability of fluorocarbon elastomers by about 100 deg, with resistance to strong oxidising agents and radiation, constitute such a system[64,106-108,110-122].

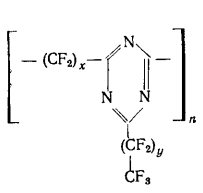
Cross-linked polymeric products containing repeating units of the above type were obtained by the thermal cyclisation of perfluoroalkylenediamidines[108]. The polycondensation of the starting materials takes place with the evolution of ammonia according to the following mechanism:



The initial diamidines were obtained by the action of ammonia on perfluoroalkyldinitriles. Perfluoroglutaronitrile yields a cyclic product—perfluoroglutaroimidine:



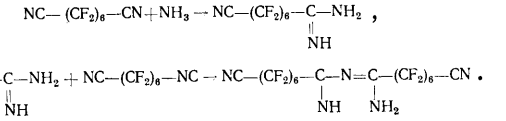
The polycondensation is usually carried out in the melt, solid infusible polymers being formed. Polymers with the following structures have been obtained from a mixture of mono- and di-functional reactants:



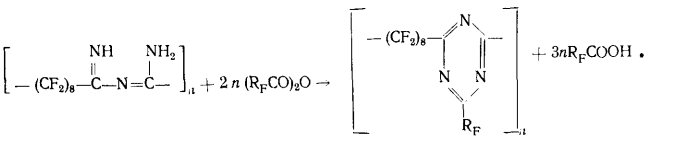
The physicomechanical properties of the cross-linked polymers of this structure depend greatly on the proportions of the initial reactants, i.e. both rubber-like materials with low strength and rigid non-elastic polymers may be obtained. The tensile strengths of these polymers vary as a rule in the range 7–35 kgf cm^{-2} with an elongation on rupture of about 100%.[108,115]

Cross-linked polyperfluoroalkylenetriazine polymers have a high thermal stability; they remain stable on heating to 420°C.[108,115] The polymers are also resistant to the action of hydrocarbon fuel and other liquid media employed in aviation up to a temperature of about 370°C; promising results have been obtained as regards their resistance to radiation[64].

It has been suggested that the development of methods for the synthesis of linear non-cross-linked triazine polymers will yield materials with improved physicomechanical properties. For this purpose, a study was made of the possible synthesis of polymers by the direct action of ammonia on the dinitrile, omitting the stages involving the synthesis and isolation of the diamidine[113]:



Together with the monocyanoamidine, a diamidine can also be formed as an intermediate. The low-molecular-weight products formed in the second stage of the reaction may be more numerous than shown in the above scheme. However, it is important that the polymerisation reaction in the presence of ammonia may be divided into two consecutive stages—the addition of ammonia to the nitrile with formation of the amidine and the addition of the latter to the nitrile in the growing chain of the imidoylamidine polymer. By adding a solution of the imidoylamidine polymer to the anhydride of a perfluoroalkanecarboxylic acid, a triazine polymer is obtained by the following mechanism:

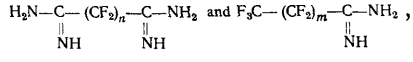


Best results were achieved when the anhydrides of trifluoroacetic, perfluorobutyric, and perfluorocaprylic acids were employed[113]. The resulting high-molecular-weight perfluorotriazine polymers were rubber-like materials soluble in ethyl perfluorobutyrate, ethyl acetate, and di(trifluoromethyl)benzene. The glass temperatures of the polymers varied in the range between −17° and −5°C. Rapid degradation began at 420°C.

Graham[119] obtained from the triazine elastomers vulcanised materials with a high strength and thermal stability up to 315°C. The polyimidoylamidine necessary for the synthesis of the elastomers was obtained by the copolymerisation of the dinitrile and diamidine of perfluorosebacic acid.

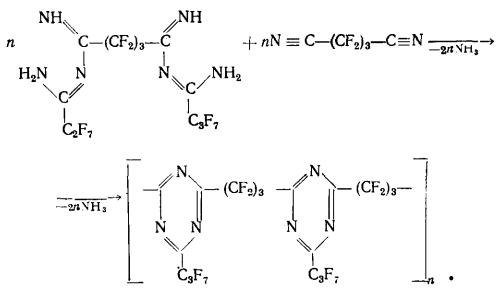
When this polymer reacted with an excess of perfluorobutyric acid anhydride, with an excess of a mixture of perfluorobutyric acid anhydride and cyanoperfluorobutyryl chloride, or a mixture of the anhydride of perfluoroacetic acid and cyanoperfluorobutyryl chloride, triazine elastomers, containing perfluoroalkyl side groups, were synthesised. The vulcanised triazine polymers are resistant to the action of strong acids but are decomposed by strong bases. The mechanical strength of these vulcanised materials, determined at an elevated temperature or after thermal ageing, is close to that of fluorocarbon vulcanisate but, in contrast to the latter, these materials remain flexible at 300° and 370°C.

Polymers with high thermal stability and satisfactory dielectric properties were obtained by the joint polycondensation of the monomers

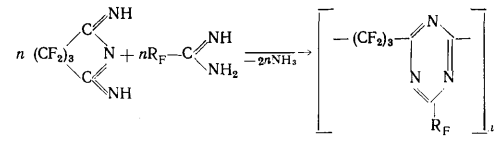


where $n = 2-4$ and $m = 2-3$, followed by vulcanisation with *p*-phenylenediamine, benzidine, triethylenetetramine, and other compounds[116].

In order to synthesise linear polyperfluoroalkylenetriazine polymers with a linear structure, a study was also made[64] of the reaction between di(perfluorobutylimidoyl)-perfluoroglutaroamidine and the dinitrile of glutaric acid:



Fedotova and Dolgopol'skii obtained polymers based on C_2–C_7 perfluoroalkylamidines and perfluoroglutaroimidines according to the mechanism



where R_F = CF_3, C_2F_5, C_3F_7, C_4F_9, or C_6F_{13}, in an attempt to elucidate the effect of the size of the perfluoroalkyl group of the monoamidine on the joint polycondensation and properties of the perfluoroalkylenetriazine polymers[120].

The principle of the method of synthesis of linear perfluoroalkylenetriazine polymers, proposed by Brown[107,108,121], is based on the joint polycondensation of mono- and di-functional perfluoroamidines. Monoamidines suppress to a considerable degree the structure-formation process but nevertheless they do not eliminate it owing to the considerable difference between the reactivities of mono- and di-functional monomers. Fedotova and Dolgopol'skii[120] showed that, starting with the C_4 amidine, the size of the perfluoroalkyl substituents has almost no influence on the properties of the polymers and the conditions of their synthesis. Moreover it was established that low-molecular-weight polymers with $[\eta]$ = 0.04–0.07 dl g^{-1}, obtained with the molar ratio monoamidine : diamidine = (1.6–1.8) : 1, are cross-linked by perfluoroglutaroimidine with formation of insoluble high-molecular-weight polymers thermostable up to 400–420°C.

The polycondensation of pentafluorobenzamidine with perfluorophthalodiamidine has been described[114].

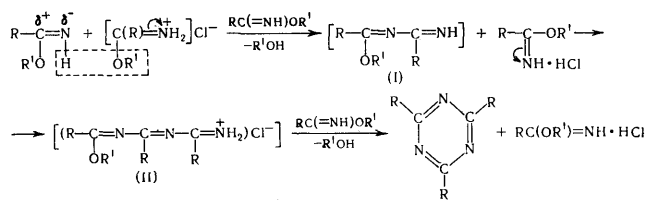
Kardash et al.[118] investigated the thermal degradation at 400–500°C of polyperfluorotriazine polymers, obtained by the copolycondensation of the diamidine of perfluorosebacic acid with perfluorobutyramidine and of perfluoroglutarodiamidine with perfluoroacetamidine. The thermal stabilities of these polymers were compared with that of polytetrafluoroethylene and it was shown that the introduction of *s*-triazine rings into the fluoromethylene chains enhances their thermal stability. However, this effect decreases to some extent in polyperfluorotriazines owing to the presence of amide groups, which increase the initial rate of degradation of the polymers. The formation of amide groups in such polymers is possible both in the synthesis of the polymers itself and during their storage, since perfluoroalkyl derivatives of *s*-triazine are hydrolysed on prolonged storage in air. The presence of amide groups in the polymers was confirmed by infrared spectroscopy (showing the C=O absorption band at 1735 cm^{-1} and the absorption bands at 3430, 3160, and 1680 cm^{-1}, which are characteristic of the NH_2 group in amides). The principal gaseous degradation product of polyperfluorotriazines is tetrafluoroethylene. In addition, hexafluoropropene, carbon dioxide, and silicon tetrafluoride, formed evidently when the CF_3 radicals react with the glass of the reaction vessel, have been identified. The liquid degradation products are low-molecular-weight analogues of polyperfluorotriazines. The water formed on decomposition of the amide groups hydrolyses the *s*-triazine rings and the radicals induce their polymerisation with formation

of the azomethine structure $[-C=N-]_n$, as in the polymerisation of 2,4,6-tri(trifluoromethyl)-*s*-triazine under the influence of radicals[109]. On the other hand, in the absence of radical sources, 2,4,6-tri(trifluoromethyl)-*s*-triazine is stable up to 500°C.[109]

Polyperfluoroalkylenetriazine elastomers are regarded as promising raw materials for the preparation of fuel tanks, electrical insulation, and rubber components of hydraulic systems operating at temperatures in the range 300–400°C.[64]

The application of perfluorinated triazine rubbers in aviation and space engineering has been described[117]. It has been stated that elastomers based on *s*-triazine, with the triazine groups linked by perfluoroalkyl units, are processed by the usual methods using standard equipment[110].

Yakubovich and coworkers[123–128] obtained polytriazines with aliphatic, aromatic, and perfluorinated aliphatic bridges between the *s*-triazine rings by the polycyclotricondensation of the corresponding iminoethers. They employed the diethyl and dimethyl esters of bisiminoadipic, bisiminoterephthalic, bisiminoperfluoroglutaric, and bisiminoperfluoroadipic acids as the starting materials for the preparation of polytriazines. Non-fluorinated iminoethers are readily cyclised in the presence of catalytic amounts of their hydrochlorides, while the fluorinated analogues react also in the absence of catalysts. Yakubovich et al.[125] believe that the condensation of iminoether groups to the *s*-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 to the more stable *s*-triazine system according to the mechanism[129]

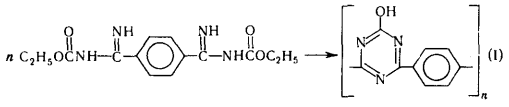


One may suppose that the electrophilicity of the carbon atom in iminoethers is insufficient to ensure the addition of a second iminoether molecule at the C=N double bond and the free bases of the iminoethers are not cyclised. When the reaction mixture contains the hydrochloride of the iminoether, in which the electrophilicity of the carbonyl carbon atom is higher than in the iminoether itself owing to the appearance of a positive charge at the nitrogen atom (the 'onium nitrogen) in $C{=}\overset{+}{N}H_2Cl$ and the associated considerable shift of the π-electron pair of the double bond, the reactivity of the system increases.

The replacement of hydrogen atoms by fluorine in the alkyl group of bisiminoethers increases the electrophilicity of the carbonyl carbon atom so much that condensation with the initial formation of the "dimer" and then of triazine derivatives occurs even in the absence of a catalyst[128].

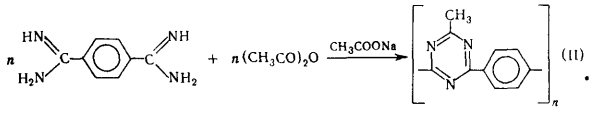
As mentioned above, for the formation of linear triazine polymers it is necessary that in the synthesis of the *s*-triazine ring one position in the latter should be occupied by a stable side group and the remaining two should participate in the formation of the polymer chain.

On this basis, Greth and Elias[61,63,130] obtained linear polytriazines by the thermal decomposition of the diethyl ester of terephthalamidine-*NN*-dicarboxylic acid:



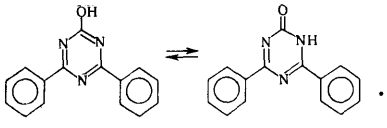
(I)

and by the interaction of terephthalamidine with acetic anhydride:



(II).

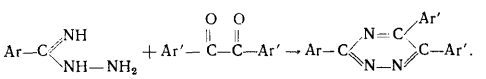
The structure of the resulting polymers was demonstrated chemically and by infrared spectroscopy (absorption bands characteristic of the *s*-triazine ring at 1540, 1450, and 1360–1390 cm^{-1}). An intense absorption band in the region of 1660 cm^{-1}, showing that these compounds may be present in the tautomeric keto-form, was observed in the spectra of poly-2-hydroxy-4,6-diphenyl-*s*-triazines:



Contrary to the authors' expectations, polytriazines obtained in this way had a much lower thermal stability than polymers synthesised by the same workers from methyltriazines and terephthalic dialdehyde[63], which were described above (see Section I, p. 70).

The temperature of the onset of decomposition in nitrogen of type (I) polymers is in the range 250–300°C. They lose 65% of their weight at 500°C and 85% at 850°C. The thermal decomposition of type (II) polymers takes place in two stages: in the first stage the decrease in weight is 12% between 200° and 325°C and in the second stage the polymer loses 50% of its weight on subsequent heating to 800°C.

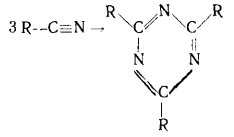
In recent years a large number of polymers with symmetrical triazine rings were synthesised and investigated; polymers containing asymmetric triazine rings were unknown until recently. A recent communication[131,132] reported the synthesis of model compounds containing asymmetric triazine rings from hydrazidines and α-diketones:



Hergenrother[133] employed this reaction to synthesise high-molecular-weight soluble poly-*as*-triazines. When 2,6-pyridinediyldihydrazidine was allowed to react with *pp'*-oxybis(phenyleneglyoxal hydrate) and *pp'*-oxydibenzil, poly[3,3'-(2'',6''-pyridinediyl)-5,5-(*pp'*-oxydiphenylene)di-(*as*-triazine)] (PT) and poly[3,3'-(2'',6''-pyridinediyl)-5,5'-(*pp'*-oxydiphenylene)di-(6-phenyl-*as*-triazine)] (PTP) were obtained. The polycondensation was carried out in *m*-cresol solution at 200°C. The resulting polymer solutions were employed without additional purification to prepare sheets, coatings, adhesives, etc. ($\eta_{log} = 0.5 = 1.25$ dl g^{-1}). The softening temperatures of the polymers were in the range 300–340°C, while according to thermogravimetric data PT and PTP exhibit the same resistance to thermal and thermo-oxidative degradation—the thermograms have a single inflection at 400°C in air and at 450°C in helium. The polymer specimens heated at 316°C for 200 h lost between 3 and 8% of their weight.

2. Polycyclotrimerisation of Monomers Containing C–N Groups

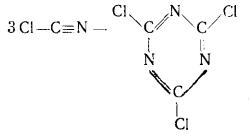
The capacity of nitriles for polymerisation with formation of triazines (the cyclotrimerisation reaction of nitriles) via the mechanism



was already known in the previous century[134,135].

Numerous subsequent studies established that the cyclotrimerisation reaction is more readily undergone by nitriles with electronegative substituents in the α-position relative to the nitrile group. Electronegative substituents in the α-position give rise to a comparatively low electron density at the carbon atom of the nitrile group and hence an enhanced electrophilic reactivity of such nitriles[136–138].

Thus chlorocyanogen is readily cyclotrimerised in the presence of various catalysts with formation of cyanuric chloride[137,139,140]:

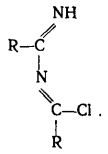


Compounds containing the C≡N group tend to form a stable cyclic trimer because trimerisation involves the loss of the enthalpy of the π bond and in addition the cyclic trimer is stabilised because of the combination of the most favourable valence angles (about 120°)[15,141] with the planar structure of the ring[15,141,142], which allows the formation of a $p\pi-p\pi$ aromatic system. The high stability of the ring in *s*-triazine is shown by the fact that many *s*-triazine derivatives do not polymerise at temperatures up to 500°C.[41]

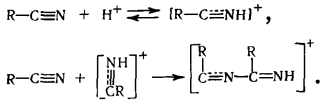
The cyclotrimerisation of nitriles may be accelerated by many catalysts. Thus the halides of coordination-unsaturated metals are active catalysts of this reaction. The presence in the C≡N: group of nitriles of a lone electron pair and also of electron-donating π bonds promotes the addition of Lewis acids to the electron pair of the nitrogen with the formation of highly electrophilic molecular compounds. Probably the addition to the nitrile of more than one equivalent of the electrophilic compound is due to the formation of the so called π-complexes[143].

Grundman et al.,[144] who investigated the mechanism of the synthesis of *s*-triazines from nitriles in the presence of hydrogen halides, showed that a compound of the nitrile

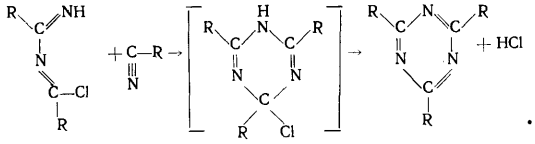
with the hydrogen halide of the type of a substituted imino-chloride,



is formed as an intermediate in this reaction. The formation of the substituted imino-chloride may be regarded as a nucleophilic reaction of the nitrile group, where the electrophilic agent is the same nitrile:

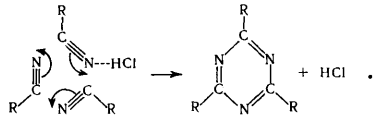


The reaction of the imino-chloride with a third nitrile molecule takes place similarly. Grundman[144] regards the interaction of imino-chlorides with nitriles as diene synthesis reactions:



However, the treatment of the adduct $2CCl_3CN.HCl$ with acetonitrile does not yield the expected *s*-triazine, although the joint cyclotrimerisation of trichloroacetonitrile with acetonitrile in the presence of hydrogen chloride leads to the formation of the corresponding di(trichloromethyl)methyl-*s*-triazine[144].

Zil'berman[138], who considered the cyclotrimerisation of nitriles, proposed a different mechanism for the formation of *s*-triazine. He believes that the reason for the comparative ease of formation of *s*-triazines may be cyclic electron transfer via the mechanism



Both the free nitrile and its complex with hydrogen halide are involved in the formation of triazines by this mechanism.

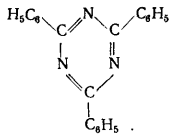
Hydrogen halides are most often employed as agents inducing the cyclotrimerisation of nitriles[136] but alkaline and acid agents, such as sulphuric and chlorosulphonic acids, Lewis acid, etc. can also serve as catalysts[136,145].

The cyclotrimerisation of benzonitrile in the presence of acid agents with formation of triphenyl-*s*-triazine (cyaphenine) has been known for a very long time[134,146-148].

Recently Kargin, Kabanov, and coworkers[149-154] carried out a number of studies on the polymerisation of nitriles via the C≡N bond in order to obtain conjugated azomethine structures. With benzonitrile as an example, they investigated the mechanism of the formation of both linear polyconjugated structures and of a cyclic trimer (triphenyltriazine).

Although the aim of these studies was not to obtain polytriazine structures, nevertheless they are of undoubted interest for the elucidation of the formation of polymers by polycyclotrimerisation and therefore some of them must be considered in this review.

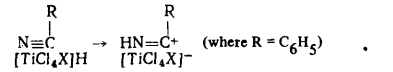
The mechanism and kinetics of the polymerisation of benzonitrile complexes in the presence of compounds such as titanium tetrachloride, zinc chloride and boron trifluoride have been investigated[150]. It has been found that, when benzonitrile complexes are heated, two types of products are formed. One of them is a polymer with an azomethine structure, $[-\underset{\displaystyle C_6H_5}{\underset{|}{C}}=N-]_n$, and the other is a benzonitrile trimer (cyaphenine):



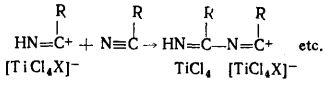
It was established that the rate of reaction and the ratio of the products formed are significantly influenced by small amounts of promoting agents such as proton-containing substances (inorganic acids, water, amides, organic acids) and organic compounds with mobile halogen atoms, for example benzoyl chloride, benzyl chloride, etc.

When the complex of benzonitrile with BF_3 is heated for 10 h at 250°, 275°, and 300°C, only the trimer with traces of a polymer is formed. The same result was obtained with the benzonitrile complex of zinc chloride. If, on the other hand, a proton initiator (HPO_3) is introduced into the reaction mixture, a polymer is formed in both cases[150].

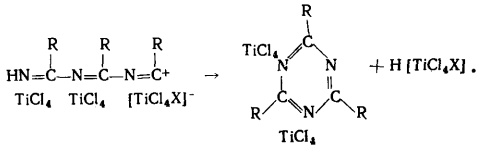
When the pure complex $(C_6H_5CN)_2.TiCl_4$ is heated in the presence of metaphosphoric acid below 300°C, the reaction proceeds at an appreciable rate, but the sole reaction product is triphenyl-*s*-triazine. At a higher temperature, a polymer is formed[153]. On the other hand, when an organic promoting agent (benzoyl chloride) is added to the system, a polymer is formed at an appreciable rate even at 270°C. The authors explain these results as follows. The centre for chain initiation is the complex $[TiCl_4X]H$ formed when the complex-forming agent reacts with the proton-containing additive:



Chain propagation takes place as follows:

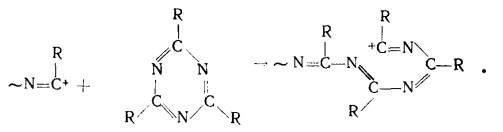


The formation and accumulation of the trimer in the initial stages of reaction can be explained by the fact that, after the addition of the third monomer molecule, there is a possibility of the formation, in addition to chain propagation, of a stable six-membered ring with regeneration of the initial initiating proton complex:



The consumption of the trimer can be accounted for by its polymerisation at an elevated temperature with the

opening of the triazine ring under the influence of the carbonium ion of the growing linear chain, which in fact leads to the formation of a polynitrile chain:

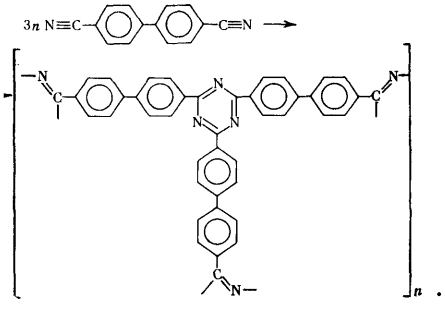


In order to test the hypothesis of the involvement of the trimer in the reaction, a study was made of the possibility of its polymerisation as a complex with $TiCl_4$, which would indeed result in a polymer with an azomethine structure.

The difference between the effects of proton-containing acids (HX) and aprotic organic acids (RX) on the linear polymerisation of benzonitrile consists in the fact that the aprotic acids are in this case more powerful promoting agents. This may be due to the higher rate of ring opening following the attack by the R^+ ion, which is a more powerful electrophilic agent than the proton[155], and to the decrease of the possibility of the cyclisation of the linear trimer when RX is employed.

Free-radical polymerisation of triazine rings is known to occur in the presence of a source of either free radicals or complex-forming agents[156]. The nature of the substituents in triazines then has a significant influence on the stability of the ring. Thus triazines with electronegative substituents (CCl_3, CF_3, and C_3F_7) form a polyene chain with conjugated double bonds $[-\underset{\displaystyle R}{\underset{|}{C}}=N-]_x$ in the presence of a source of free radicals at 250–300°C, while triazines with electropositive substituents (CH_3, C_2H_5) are polymerised only at 520°C.[156]

The cyclotrimerisation of nitriles with the aim of synthesising polytriazines was achieved for the first time by Anderson and Holovka[44], who obtained thermostable polymers with triazine rings from aromatic dinitriles under the influence of chlorosulphonic acid:

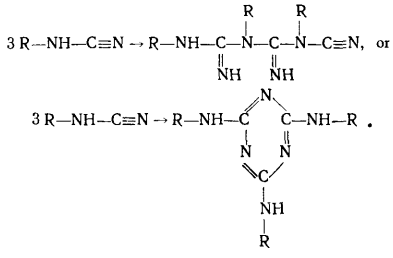


The polycyclotrimerisation of, for example, 4,4′-dicyanobiphenyl was continued until the characteristic absorption band of the C≡N bond disappeared from the infrared spectra of the polymer. In order to confirm the structure of the polymer obtained from 4,4′-dicyanobiphenyl, it was hydrolysed in the presence of concentrated hydrochloric acid and biphenyl-4,4′-dicarboxylic acid was identified. According to thermogravimetric data, the polymer synthesised exhibits a high thermal stability up to 350–400°C.

For comparison, Anderson and Holovka[44] synthesised a number of aromatic melamine polymers by the polycondensation of cyanuric chloride with aromatic diamines. All the polymers showed a high thermal stability (up to 400°C) and the polymer based on ring-fluorinated aromatic diamines was stable up to 500°C.

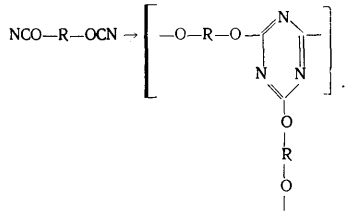
The polymerisation of 2,4,6-tricyano-*s*-triazines, which may result in the formation of both polyazomethine and polytriazine structures, has been reported[157]. These polymers, which have semiconducting properties and are used to manufacture thermistors, are obtained by heating a mixture of 2,4,6-tricyano-*s*-triazine in an excess of quinoline at the boiling point of the latter.

Sugino et al.[158–163] obtained polymers from alkylenedicyanamides with the general formula $N\equiv C-NH-(CH_2)_m-NH-C\equiv N$, where m = 4–10. Compared with nitriles having a similar structure, the C≡N groups of cyanamides are much more reactive, which may be due to the higher electrophilicity of the carbon atoms in this group. Alkylenedicyanamides are readily polymerised below 100°C and slowly at room temperature with formation of infusible and insoluble polymers. The authors believe that the polymers obtained may have the structure of polydicyanodiamides or polymelamine, which may be represented as follows for monocyanamide as an example:



Cyanamide polymers may be used to prepare ion-exchange resins, transparent plastics, coatings, and also adhesives for glass, metals, ceramics, and wood[159–163]. The strength of the joint produced by sticking together glass with these polymers is 400 kgf cm^{-2}.[162,163]

Grigat et al.[164,165] obtained cross-linked poly(aryl cyanurates) by the polycyclotrimerisation of various dicyanate esters of bisphenols via the mechanism

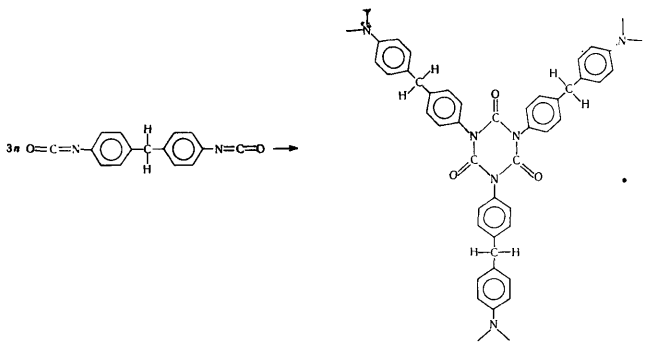


The starting materials employed were the dicyanate esters of resorcinol, quinol, 2,2-di-(4-hydroxyphenyl)propane, and 2-nitroresorcinol. The resulting cross-linked poly(aryl cyanurates) had fairly satisfactory physicomechanical properties [specific impact strength about 20 kgf m cm^{-2}, ultimate bending strength 1300–1800 kgf cm^{-2}, thermal stability (after Martens) up to 212–240°C].

The polycyclotrimerisation process was carried out in several stages. In the initial polymerisation stages fusible and soluble pre-polymers were obtained, and were converted into an infusible and insoluble state on heating to 200–250°C.

The presence of stable aromatic systems between oxygen atoms (–R–) in similar structures promotes the synthesis of polymers with even higher heat resistance and thermal stability[166].

Ball et al.[167] described the results of technical tests on a rigid isocyanurate foam plastic, which they obtained by the cyclotrimerisation of di(isocyanatophenyl)methane:



The cyclotrimerisation reaction was regulated by basic catalysts. The temperature of the onset of decomposition of the isocyanurate foam plastic is in the region of 300°C according to thermogravimetric analysis in air. The isocyanurate foam plastic exhibits a higher fire resistance than the usual urethane foam plastics, due to the formation on its surface under the influence of flames of a carbonaceous fibrillar network, reproducing the initial structure of the foam. The isocyanurate charcoal formed breaks down very slowly even at 1200°C.

The kinetics of the cyclotrimerisation of di-isocyanates were investigated by Petrov et al.[168] using infrared spectroscopy. They studied the "pre-polymer" obtained by the reaction of one mole of low-molecular-weight polybutadiene (M = 4000) containing terminal OH groups with two moles of 2,4-tolylene di-isocyanate. The catalyst components were glycidyl phenyl ether and benzyldimethylamine in different molar proportions.

The authors showed that the cyclotrimerisation of isocyanate groups is a quasi-unimolecular reaction up to a conversion of 70–90%. The rate of cyclotrimerisation is directly proportional to the product of the initial concentrations of the tertiary amine and the epoxy-derivative of the olefin.

It has been suggested that the cyclotrimerisation reaction is a special case of anionic polymerisation[168].

The results obtained were explained by Beitchman's stepwise mechanism[169], according to which the addition of the first, second, and third isocyanate molecules (M) to the catalytic complex (N) takes place in the same manner:

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

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

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

However, it was noted that, although according to Beitchman's mechanism the closure of the isocyanate rings with elimination of the catalyst is most likely in the trimer stage, other reactions are possible in principle, for example the partial formation of the dimer or of a linear polymer.

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The s-triazine ring, which has aromatic properties, exhibits high thermal stability, approaching that of the benzene ring[41,170]. Therefore, when polytriazines contain fairly thermostable groups (phenyl groups, fluorinated aliphatic chains, etc.) binding and surrounding the s-triazine rings, the polymers show enhanced thermal stability.

The ready availability of the starting materials for the synthesis of the majority of polytriazines and also the versatility of the synthetic reactions (particularly the use of polycyclotrimerisation and polycyclocondensation reactions) have promoted a large-scale practical application of these polymers in the newest branches of engineering, where materials with enhanced thermal stability and heat resistance are required. Polytriazines are used as thermostable elastomers, as binders for reinforced plastic, adhesives, coatings resistant to ultraviolet irradiation, etc.

During the preparation of the manuscript for the press, a number of interesting studies on the synthesis and properties of polymers containing s-triazine rings were published.

Polycondensation of monomeric s-triazine derivatives yielded polyesters[171-179], polyamides[180-183], and other polymers of different classes[184-192]. The thermal degradation of certain polymers containing triazine rings in the chain was investigated[193-197].

New data were published on the synthesis and properties of triazine polymers synthesised by the polymerisation of unsaturated side groups[198-209] and polymers obtained by the migration copolymerisation[210-217] of s-triazine derivatives.

Interesting results are reported in studies published recently on the polycondensation of nitrile derivatives[218-228].

A number of studies have been made on the linear polymerisation of nitriles[229-232] and the polymerisation of s-triazine rings with formation of polymers having the azomethine structure.

New results have also been obtained in the study of the polycyclotrimerisation of nitriles of different structures[235-239], cyanate esters[240-242], and isocyanates[243-250].

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Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow