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The Synthesis of Polycyanates by the Polycyclotrimerisation of Aromatic and Organoelement Cyanate Esters

V.A.Pankratov, S.V.Vinogradova, and V.V.Korshak

Studies on the synthesis and properties of a new class of heat-resistant and thermostable polymers, obtained by the polycyclotrimerisation of aromatic and organoelement cyanate esters, are examined. Attention has been concentrated on studies devoted to the given reaction, the influence of the structure of polycyanates on their properties, and the specific features of these polymers due to the regularity of their structure. A number of general characteristics of polycyclotrimerisation, i.e. its usefulness as a method of synthesis of cross-linked thermostable polymers, are discussed. The bibliography includes 160 references.

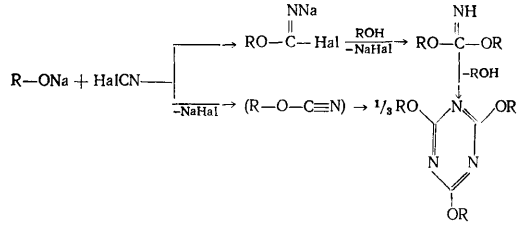
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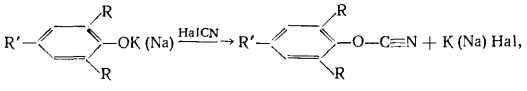
I. INTRODUCTION

Cyanic acid HO–C≡N is involved in 1,3-prototropic tautomerism with isocyanic acid O=C=NH as a result of which esters of both cyanic acid (R–O–C≡N, cyanates) and the isomeric esters of isocyanic acid (R–N=C=O, isocyanates) are known. However, whereas isocyanates were discovered by Wurtz in the initial period of the development of organic chemistry in 1849,[1] the first examples of cyanates were synthesised by Stroh and Gerber as late as 1960.[2] Isocyanates assumed practical importance only 100 years after their discovery. Judging from the vigorous development of research on the chemistry of cyanates, one may predict with confidence that the corresponding period for these substances will be much shorter.

The attempts to synthesise cyanate esters were begun in 1857[3-13]. In the main, investigators tried to solve this problem by the reaction of phenoxides (or alkoxides) with halogenocyanogens[3-11], but cyanate esters were not isolated and the main reaction products were cyanuric acid esters. It was shown that an imino-ester of carbonic acid is formed as an intermediate under these conditions[9,13] and that the reaction mechanism can be represented as follows:

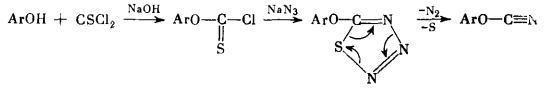


Nevertheless Stroh and Gerber[2] and later other investigators[14,15] succeeded in synthesising cyanate esters in this way from sterically hindered phenols:

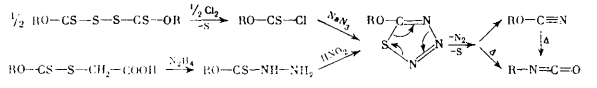


where R = t-C_4H_9 and R′ = C_6H_5.

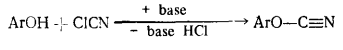
It was not until 1964 that several new methods of synthesis of compounds of this class were proposed[16-22]. Martin and coworkers[16-19] obtained aromatic and then aliphatic cyanates by the thermolysis of 1,2,3,4-thiatriazoles via the following mechanism:



Jensen and Holm[20,21] achieved the synthesis of aliphatic cyanates using a somewhat different scheme:



A method of synthesis of cyanate esters from phenols and acid alcohols involving their interaction with a halogenocyanogen in the presence of a hydrogen halide acceptor, which is promising from the standpoint of its application in industry, has been proposed by Grigat and Pütter[22]:



The reaction takes place at temperatures between −20° and +20°C in an organic solvent (for example acetone) and the yields of cyanates are nearly quantitative.

A number of other methods of synthesis of cyanates have been described in the literature[23-28], but they suffer from disadvantages such as a large number of stages and low yields, as a result of which they are less promising for practical purposes.

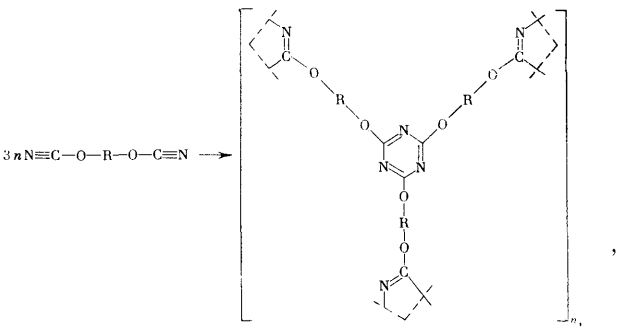
Bearing in mind that a number of reviews on the synthesis and properties of cyanate esters have already been published[29-34], we shall not concern ourselves in the present review with this field and attention will be concentrated on polymers based on cyanates and the processes leading to their formation.

The studies in the field of polymers based on cyanate esters developed only in the last decade. However, a sufficient number of data on these polymers, which are of interest from both theoretical and practical points of view, are already available and need to be surveyed. This applies particularly to research on the polycyclotrimerisation of cyanates, which has led to the discovery of many interesting general features of this new and promising method of synthesis of cross-linked thermostable polymers.

Studies on the polycyclotrimerisation of cyanate esters have been mainly designed to investigate the features of this reaction and the synthesis of new structures as well as various properties of polycyanates. The literature data have been reviewed in the same order in the present article. In addition, we shall consider also the few studies described in the literature on the synthesis of other less thoroughly investigated cyclopolymers based on cyanate esters.

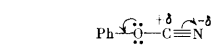
II. THE CHARACTERISTICS OF THE POLYCYCLOTRIMERISATION REACTION OF CYANATE ESTERS

The polycyclotrimerisation reaction of dicyanate esters with formation of cross-linked polymers (polycyanates) proceeds via the mechanism:



where R are different aromatic and organoelement groups.

Aryl cyanates are more reactive than nitriles because of the more electrophilic properties of the carbon in the N≡C group owing to the electron-accepting effect of the aryloxy-group[35,36]. Martin and Brause[36] established that the oxygen atom in the compounds HR–O–C≡N has an electron-donating effect on the aromatic group and at the same time enters into mesomeric interaction with the carbon of the nitrile group. However, the involvement of the unpaired electrons of oxygen in the mesomerism of the ring is greater than in the mesomerism of the nitrile group of aryl cyanates:



which promotes the enhancement of the electrophilic properties of the carbon of the N≡C group.

At the same time, like nitriles, aryl cyanates exhibit nucleophilic properties due to the presence in the N≡C group of the lone electron pair of the nitrogen atom and of electron-donating π-bonds. The cyclotrimerisation of cyanates is therefore accelerated by catalysts of both anionic and cationic type, depending on whether the nucleophilic nitrogen atom or the electrophilic carbon atom is attacked.

In recent years, Korshak and coworkers[37,38] put forward the concept of the heterogeneity of polymer linkages owing to the occurrence of a number of side reactions, apart from the main reaction involving the formation of the polymer system. Such "defectiveness" of the structure of a particular polymer leads in most cases to an impairment of properties such as heat resistance and thermal stability, physicomechanical parameters, etc.

It has been shown in many studies on the polymerisation of isocyanates, ethynyl derivatives, nitriles, and other compounds that the polycyclotrimerisation of these compounds involves, apart from the main process, numerous side reactions (chain polymerisation, dimerisation, etc.). Methods of synthesis excluding these side reactions have not so far been found[39-52] and the synthesis of polymers with a virtually defect-free structure is an urgent problem whose solution will permit a considerable improvement of many of their parameters and may lead to the formation of materials with qualitatively new properties.

A high selectivity in the cyclotrimerisation of the N≡C–O groups is characteristic of the polycyclotrimerisation of dicyanates with formation of cross-linked polymers. This is one of the fundamental features of the polycyclotrimerisation of these groups, which distinguishes them from other functional groups, such as the nitrile, isocyanate, ethynyl, etc. groups.

Furthermore, an exceptionally important feature is that, when the process is carried out under certain conditions, the cyclotrimerisation of the N≡C–O groups of tricyanates proceeds with virtually quantitative conversion. All these factors promote the achievement of "pure" polycyclotrimerisation with few defects and the formation of highly cross-linked polymers with a regular chemical structure[53-65].

Indeed the cyclotrimerisation of monofunctional cyanate esters led to the isolation of cyanurates in quantitative yields and no side products (dimers, linear polymers, etc.) could be detected chromatographically or by other methods[29,30,55,57,58]. Comparison of the spectroscopic and other characteristics of the polymers, obtained by polycyclotrimerisation and by specific synthesis from cyanuryl chloride and bisphenols, demonstrated their complete identity[54,55]. The absence of the signal characteristic of polyconjugated systems from the ESR spectra of polycyanates fails to confirm the possibility of the linear polymerisation of the N≡C groups of cyanates[55]. Furthermore, in the study of the polymerisation of dicyanates by infrared spectroscopy, it was not possible to detect either the dimerisation or isomerisation of the N≡C–O group; the infrared spectra did not contain absorption bands characteristic of linear acomethine structures either. In the discussion of the properties of polycyanates below, we shall consider also other direct and indirect evidence indicating the high selectivity of the cyclotrimerisation of NCO groups in the synthesis of these polymers.

One must nevertheless stipulate that the possibility of side reactions cannot of course be fully ruled out in the polycyclotrimerisation of aromatic cyanate esters. However, bearing in mind the entire set of the available literature data on this process, these reactions presumably take place to only a slight extent.

The comparative catalytic activities of various protic and aprotic acids and bases as well as their mixtures were investigated, using as an example 2,2-di-(4-cyanatophenyl)-propane, in the bulk polycyclotrimerisation of aryl dicyanates[56]. It was found that in the initial stages the polycyclotrimerisation of the N≡C–O groups of aryl dicyanates obeys the relations of the quasi-unimolecular reaction. The rate constants and activation energies for this process, carried out in the presence of various types of catalysts, were calculated and it was shown that the catalytic activities of tertiary amines and phenols are proportional to their pK_a values and increase with the basicity of amines and the acidity of phenols. The corresponding correlations have been deduced.

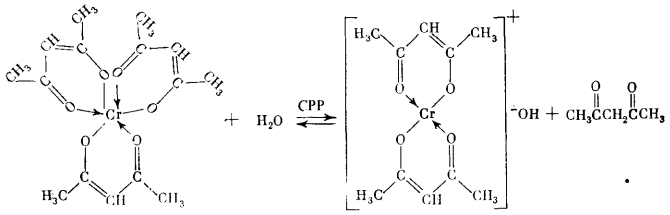
The influence of the chemical structure of initial dicyanates of the type

where A = CH_2, $C(CH_3)_2$, $C(CF_3)_2$, CHC_6H_5, or $C(CH_3)(C_6H_5)$, on their reactivity in polycyclotrimerisation in the presence of zinc chloride has been investigated and it has been shown that the rate of the process in the first stage is determined by the inductive effect of the substituents at the central carbon atom of the initial dicyanate, increasing as they become more electronegative. At more advanced stages of the reaction of the N≡C–O groups of the dicyanate, the rate depends also on the steric factors of the substituents at the central carbon atom of the dicyanate[56].

A series of studies by Bonetskaya and coworkers[57,59-62] were devoted to a detailed investigation of the kinetics and heats of the cyclotrimerisation and polycyclotrimerisation of aryl cyanates. Thus the kinetics of the cyclotrimerisation of phenyl isocyanate to triphenyl cyanurate have been investigated in solution in ditolylmethane in the presence of chromium(III) acetylacetonate with the aid of a double calorimeter[57] and it was shown that the reaction is autocatalytic. Its maximum rate is proportional to the catalyst concentration and the square of the monomer concentration. The heat of cyclotrimerisation of phenyl cyanate was determined as $\Delta H = -28.1 \pm 1.0$ kcal mole^{-1}. The stabilisation energy of the *s*-triazine ring has also been estimated and it has been noted that the ring is stabilised both as a result of the delocalisation of electrons with formation of a system resembling the π-electron system of the benzene ring and by the partial polarisation of the ring nitrogen–carbon bond. In order to estimate the stabilisation energy of the *s*-triazine ring, the experimental heat of the cyclotrimerisation of phenyl cyanate (PC) to triphenyl cyanurate (TPC) was compared with the heat of this reaction in the gaseous state ($\Delta H = -58.2$ kcal mole^{-1}). The latter quantity was calculated from the heats of formation of phenyl cyanate and triphenyl cyanurate evaluated additively from the increments for the corresponding groups[66] ($\Delta H_f = 29.7$ and 30.9 kcal mole^{-1}). The authors regard the difference $\Delta H = 26$ kcal mole^{-1} between the experimental and theoretical heats as the stabilisation energy of the *s*-triazine ring (the stabilisation energy of the benzene molecule is approximately 36 kcal mole^{-1}).[57]

The kinetics of the polycyclotrimerisation of 2,2-di-(4-cyanatophenyl)propane (CPP) have been investigated and its heat measured by direct calorimetric determinations under conditions analogous to those of a model reaction[59-61]; it was established that the polycyclotrimerisation of CPP involves mainly the same kinetic features as the cyclotrimerisation of phenyl cyanate. The average heat of polycyclotrimerisation of CPP is[59,60] $\Delta H = -56.8$ kcal mole^{-1}, i.e. 28.4 kcal mole^{-1} per N≡C–O group. The close agreement of this value with the heat of cyclotrimerisation of phenyl isocyanate ($\Delta H = -28.1$ kcal mole^{-1}) confirms, according to the author, the high selectivity of the polycyclotrimerisation of aryl dicyanates.

The cyclotrimerisation of aryl cyanates in the presence of chromium(III) acetylacetonate is autocatalytic (the variation of the rate with time passes through a maximum), although the reaction products [triphenyl cyanurate when phenyl cyanate is the starting material and oligomers in the polycyclotrimerisation of 3,2-di-(4-cyanatophenyl)propane] do not catalyse the process[57,59-62]. One of the causes of autocatalysis is probably the fact that chromium(III) acetylacetonate is catalytically inactive in the initial state. It was established[59] that the presence of traces of water in the reaction system has an appreciable influence on the rate of polycyclotrimerisation of CPP and traces of acetylacetone in the reaction mass after the latter had been thermostatted at 140°C were detected by gas–liquid chromatography. It was found that the addition of water to the reaction system increases and that of acetylacetone decreases the rate of reaction[62]. The results suggested that the active form of the catalyst is formed with participation of water and is in equilibrium with the normal form of the catalyst:



The autocatalytic nature of the cyclotrimerisation of aryl cyanates in the presence of chromium(III) acetylacetonate is associated with the accumulation of the active form of the catalyst as the reaction proceeds.

The enthalpy, entropy, and Gibbs free energy of the polycyclotrimerisation of crystalline and liquid CPP to a regularly cross-linked amorphous polymer have been calculated[63] (Table 1). The enthalpy of polymerisation found at 420 K (147°C), i.e. $-\Delta H_{pol} = 53.2$ kcal mole^{-1}, agrees within the limits of experimental error with the enthalpy of polymerisation determined by direct calorimetric measurements ($-\Delta H_{pol} = 56.8$ kcal mole^{-1}),[60] which confirms yet again that the polycyclotrimerisation of aryl dicyanates always proceeds in the same way. The decrease of entropy on polymerisation with formation of cross-linked systems, determined for the first time by Lebedev et al.,[63] proved to be −36 e.u., which is approximately 30% larger than for linear polymerisation.

Table 1. Thermodynamic parameters of the polycyclotrimerisation of 2,2-di-(4-cyanatophenyl)propane*.

T, K	$-\Delta H^\circ_{pol}$, kcal mole^{-1}	$-\Delta S^\circ_{pol}$, kcal mole^{-1} K^{-1}	$-\Delta G^\circ_{pol}$, kcal mole^{-1}
	Monomer(c) ⇌ polymer(g)		
100.00	44.5	7.88	43.7
200.00	45.2	12.7	42.7
298.15	45.9	15.5	41.3
355.83	46.2	16.4	40.3
	Monomer(l) ⇌ polymer(g)		
355.83	52.5	34.1	40.3
400.00	52.9	35.9	38.8
420.00	53.2	35.9	38.1

*The physical state of the monomer and polymer is indicated in brackets: c—crystalline; g–glass; l–liquid.

Table 1 shows that, in the temperature range 100–420 K, $\Delta H^\circ_{pol} < 0$ and $\Delta S^\circ_{pol} < 0$, which implies that CPP is a monomer with an upper limiting polymerisation temperature of 1480 K, i.e. much higher than the temperature of the onset of the thermal decomposition of the monomer and polymer. (Below 1480 K, there are no thermodynamic obstacles to the conversion of the monomer into a polymer, while above this temperature the polymer cannot be obtained.)

The absolute value of ΔG°_{pol} shows that the equilibrium in the polymerisation reaction is almost completely displaced towards the formation of the polymer[63].

III. INDIVIDUAL EXAMPLES OF POLYCYANATES

1. Homopolymers of Aromatic and Organoelement Dicyanate Esters

Table 2 presents the structures and melting points of di- and tri-functional aromatic and organoelement cyanate esters described in the literature as well as certain thermal characteristics of the polymers based on them. In most cases the monomers are crystalline substances with melting points much lower than those of the hydroxy-compounds from which they were obtained. Certain organoelement dicyanates (see Nos. 33 and 34, Table 2) are liquids at these temperatures. The temperatures of the onset of deformation (from thermomechanical curves) and the temperatures of the onset of decrease in weight (from thermogravimetric data obtained in air) are quoted in Table 2 as the thermal characteristics whereby a comparative assessment of the polymers is possible. Unfortunately there are no data on the behaviour of a number of polycyanates, which have been described largely in patents, at elevated temperatures.

Table 2. Di- and tri-functional aromatic and organoelement cyanates and the thermal characteristics of the polymers based on them.

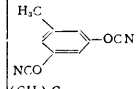
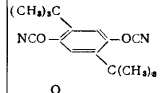
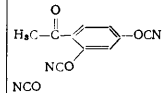
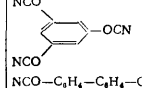
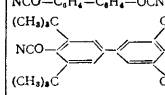
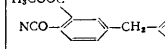
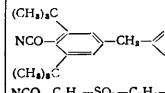
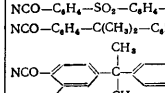
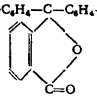
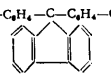
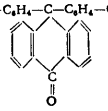
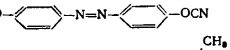
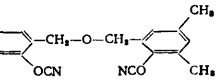
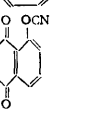
No.	Initial cyanate	M.p., °C	$T_{o.d.}$, °C*	$T_{w.l.}$, °C**	References
1	m-NCO–C_6H_4–OCN	78–79,5	360	390	22,30,53,67–69
2	p-NCO–C_6H_4–OCN	115–116	395	390	22,30,53,67–69
3		72–74	—	—	30
4		130	—	—	70,71
5		78–80	—	—	72
6		102	—	—	22,30
7	NCO–C_6H_4–C_6H_4–OCN	133–133,5	380	390	30,54
8		263	—	—	30
9	NCO–C_6H_4–O–C_6H_4–OCN	88–89	400	380	54
10	NCO–C_6H_4–CH_2–C_6H_4–OCN	107.5–108	370	400	53,69
11		100–101	—	—	30
12		206	—	—	2,30
13	NCO–C_6H_4–SO_2–C_6H_4–OCN	182–183	360	360	30,54
14	NCO–C_6H_4–$C(CH_3)_2$–C_6H_4–OCN	81.5–82	385	385	30,53,54,69
		77–78	280	330	54
15					

Table 2 (Cont'd).

No.	Initial cyanate	M.p., °C	$T_{o.d.}$, °C*	$T_{w.l.}$, °C**	References
16	NCO–C_6H_4–$C(CF_3)_2$–C_6H_4–OCN	87.5–88	360	395	53,54,69
17	NCO–C_6H_4–$C(H)(C_6H_5)$–C_6H_4–OCN	72.5–73	410	410	53,54,69
18	NCO–C_6H_4–$C(CH_3)(C_6H_5)$–C_6H_4–OCN	87–88	370	395	53,54,69
19	NCO–C_6H_4–$C(C_6H_5)_2$–C_6H_4–OCN	190.5–191.5	360	400	53,54,69
20	NCO–C_6H_4–C–C_6H_4–OCN	134–135	385	405	53,54,69
					
21	NCO–C_6H_4–C–C_6H_4–OCN	162.5–163	375	400	53,54,69
					
22	NCO–C_6H_4–C–C_6H_4–OCN	169–170	395	400	53,54,69
					
23	NCO–	163	—	—	71
24		107–108	—	—	30
25	NCO–	infus.	—	—	30
26		infus.	—	—	30
27		149	—	—	30
28	NCO–C_6H_4–C(–$B_{10}H_{10}$)–C–C_6H_4–OCN	158–159,5	370	370	73
29	NCO–C_6H_4–CH_2–C(–$B_{10}H_{10}$)–C–CH_2–C_6H_4–OCN	152–153	370	370	74,75
30	NCO–CH_2–C(–$B_{10}H_{10}$)–C–C_6H_4–C(–$B_{10}H_{10}$)–C–CH_2–OCN	135–136	300	380	76,77
31	NCO–CH_2–C(–$B_{10}H_{10}$)–C–CH_2–OCN	127.5–128	280	360	78,79
32	m-NCO–CH_2–$CB_{10}H_{10}C$–CH_2–OCN	63–64	290	370	78,79
33	NCO–CH_2–$(CF_2)_3$–CH_2–OCN	—	350	360	80,81
34	NCO–CH_2–$(CF_2)_4$–CH_2–OCN	—	340	350	80,81

* Here and henceforth the temperature of the onset of deformation ($T_{o.d.}$) was determined from the thermomechanical curve for a load 0.8 kgf cm^{-2} and a heating rate of 80 k h^{-1}.

** The temperature of the onset of weight loss ($T_{w.l.}$), obtained from thermogravimetric analysis (heating rate 4.5 K min^{-1}), was assumed to be the temperature corresponding to the point of intersection of the tangents to the curve in the region where weight loss begins.

The polycyanates listed in Table 2 are highly cross-linked heterochain polymers the nodes of the networks of which consist of *s*-triazine rings, while the internodal fragments comprise the residues of aromatic bisphenols, polyphenols, and organoelement glycols and phenols. The data in Table 2 show that the presence of these thermally stable groups in the polycyanate structure promotes a high thermal stability of the latter. Furthermore, the results obtained in thermomechanical studies on polycyanates have demonstrated (see Table 2) that the temperatures of the onset of deformation are in most cases in the region close to the temperatures of the onset of weight loss, i.e. the

heat resistance of these highly structured rigid systems is limited by their thermal stability. The thermal, physicomechanical, and other properties of the most interesting polycyanates will be discussed below.

There are no literature data on polycyanates with unsubstituted aliphatic internodal fragments. Presumably the presence of flexible polymethylene chains in place of rigid aromatic rings in the polycyanate structure should have promoted an increase of the elasticity of these materials but, naturally, it would have been accompanied by some decrease of the thermal stability of the polymers. It is noteworthy that the initial monomers for such polymers, aliphatic cyanate esters, cannot be obtained from glycols and halogenocyanogens; on heating, they also readily isomerise to isocyanates[29].

It has been found that the hypothetical structures of polycyanates with aliphatic internodal fragments can be achieved by the introduction of perfluoro-groups in the α-position relative to the cyanate group. Such fluorine-containing mono- and di-cyanates were obtained for the first time[81] by the reaction of the corresponding alcohols with chlorocyanogen in the presence of triethylamine. These cyanates are resistant to isomerisation and polymerise readily with formation of polymers whose thermal stability is not inferior to that of aromatic polycyanates[80]. Depending on the proportions of the mono- and di-cyanates taken for copolymerisation, polymers with glass points between $-40°$ and 350°C were obtained. They can be used as thermostable films, adhesives, and elastomers with improved fire resistance[80].

One of the most interesting examples of organoelement polycyanates comprises polymers containing carborane groups in the internodal fragments. A report on the synthesis of carborane-containing aliphatic cyanates based on 1,2- and 1,7-dihydroxymethylcarboranes was published in 1971.[78] In contrast to the usual aliphatic cyanates, the N≡C–O groups of these compounds proved to be resistant to isomerisation to the O=C=N groups. The resistance to isomerisation in such cases, as well as that of fluorine- and chlorine-containing cyanates[30,81], can be accounted for by the large negative inductive effect of the carborane ring, transmitted via the methylene bridges[78]. Subsequently dicyanate esters of other carborane-containing glycols and bisphenols were synthesised and polymers based on them were described[73-77].

Table 3 presents the structures of carborane-containing dicyanates and certain properties of their polymers. A characteristic feature of polymers based on dicyanatomethylcarboranes is lower heat resistance compared with aromatic polycyanates, but, as regards the temperature of the onset of weight loss, they are similar to their carbocyclic analogues[79]. The most interesting property of these polymers is the large amount of carbon-containing residue at elevated temperatures (between 500° and 1000°C), frequently with retention of a definite strength.

Like aromatic analogues, carborane-containing polymers are characterised by high physicomechanical parameters (specific impact strength up to 30 kgf cm cm^{-2}, bending strength up to 1700 kgf cm^{-2}, Brinell hardness up to 1500 kgf cm^{-2}, etc.); they can be readily converted into manufactured articles by the usual methods for working with thermoreactive polymers without the evolution of volatile materials[73-79]. Their conversion into manufactured articles is facilitated also by the fact that the initial monomers have relatively low melting points, ranging from 63°C (*m*-dicyanatomethylcarborane) to 158°C (1,2-dicyanatodiphenylcarborane).[73-79]

Owing to the strong adhesion of carborane-containing cyanates to various materials and other properties of practical value, which are indicated above, these polymers are used as heat resistant and thermostable films, coatings, binders for glass-fibre-reinforced plastics, adhesives, etc., particularly when a high resistance to ablation is necessary[73-79]. Large carbon-containing residues have been observed up to 1000°C for carborane-containing polycyanates not only when the latter were thermostatted in air but also in an inert atmosphere. Thus the polycyanate based on 1,2-di-(4-cyanatophenyl)carborane loses 2% of its weight in air at 900°C and 16% at the same temperature in an atmosphere of helium. In view of the low availability at the present time of carborane-containing monomers, it is of considerable interest that small amounts of added carborane-containing cyanates appreciably increase the thermal stability of polycyanates when they are copolymerised with the usual aromatic dicyanates[82]. Thus, whereas the polymer based on 2,2-di-(4-cyanatophenyl)propane without a carborane-containing additive loses 58% of its weight on heating in air for 1 h at 350°C, the weight loss by the polycyanates to which 0.25 mole % of 1,2-dicyanatodiphenylcarborane has been added amounts to 27%.[82]

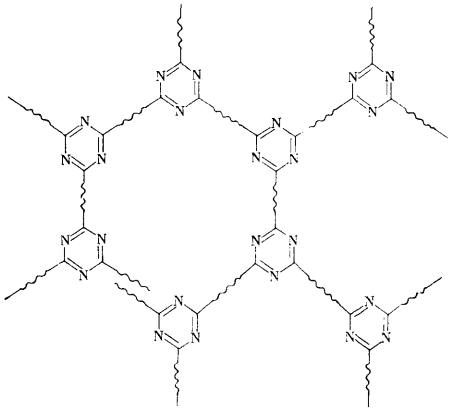
Table 3. Properties of carborane-containing polycyanates.

No.	Initial dicyanate	Properties of polycyanates: boron content, %	$T_{o.d.}$, °C	$T_{w.l.}$ in air, °C	coke residue at 900°C, %	References
1	$NCOCH_2-C_2B_{10}H_{10}-CH_2OCN$	42.53	280	360	105	78,79
2	m-$NCOCH_2-CB_{10}H_{10}C-CH_2OCN$	42.53	290	370	110	78,79
3	p-$NCOCH_2-CB_{10}H_{10}C-CH_2OCN$	42.53	310	350	102	79
4	$NCOC_6H_4-C_2B_{10}H_{10}-C_6H_4OCN$	28.58	370	370	98	73
5	$NCOCH_2-C_2B_{10}H_{10}-C_6H_4-C_2B_{10}H_{10}-CH_2OCN$	45,71	370	370	92	76,77
6	$NCOC_6H_4CH_2-C_2B_{10}H_{10}-CH_2C_6H_4OCN$	26.67	370	380	92	74,75

2. Polycyanates Based on Oligomers with Terminal Cyanate Groups

Apart from polymers based on low-molecular-weight monomeric dicyanates, polymers obtained by the polycyclotrimerisation of oligomeric dicyanate esters are of considerable interest because it is possible to regulate easily in this way both the length and the chemical structure of the internodal fragment, achieving thereby the specific synthesis of polymers with a particular set of properties.

As for the polycyanates discussed above, the structure of the polymers obtained from oligomeric dicyanate esters consists of a trifunctional network with *s*-triazine rings at its nodes; the internodal distance is determined by the length of the initial oligodicyanate:



There are interesting data for polycyanates based on mono- and di-cyanates containing oligomeric fluoroalkylene and fluoroalkylene oxide linkages having the general formula[83]

$$F_3C(CFX)_aA(CFX)_bCH_2OCN \text{ and } NCOCH_2(CFX)_aB(CFX)_bCH_2OCN,$$

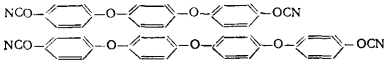
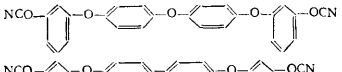
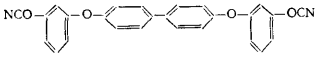
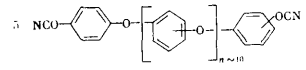
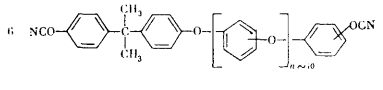
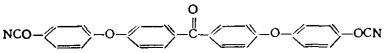
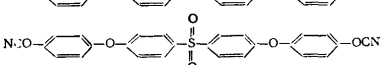
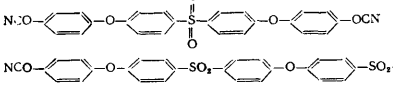
where X = fluorine or perfluoroalkyl while A and B are a C–C bond or an $O(CFXCF_2O)_c$ group. These polymers are distinguished by resistance to the action of solvents and are used for impregnation and as adhesives, films, and binders for rocket fuel.

A number of polymers based on oligoarylene oxides with terminal cyanatophenyl groups have also been described in patents[84,85] (Table 4). The initial bisphenols were obtained by the Ullmann stepwise condensation of the corresponding aromatic dihalogeno-compounds with potassium methoxyphenoxide and subsequent hydrolysis of the methoxy-groups. The authors achieved the homopolymerisation of the dicyanates of oligoarylene oxides as well as their copolymerisation with aliphatic perfluorocyanates by heating the reactants at 50–200°C[84,85]. It was noted that the polymerisation temperature may be reduced to 25–100°C in the presence of catalysts, which were $AlCl_3$, BF_3, $FeCl_3$, $TiCl_4$, $ZnCl_2$, protic acids such as HCl, the salts of weak acids (NaOAc, NaCN, KSCN, and $NaHCO_3$), as well as basic compounds, for example NaOMe, KOH, pyridine, and triethylamine. The polymers obtained have a high thermal stability and rigidity and can be used as adhesives, coatings, and binders. The ultimate shear strength of the aluminium–aluminium adhesive seam, formed using the dicyanates[84] hardened for 1 h at 177°C and a pressure of 2 atm, are presented in Table 5.

Table 5. The ultimate strengths of the Al–Al adhesive seam formed using oligoarylene oxide dicyanates as the adhesives[84].

No. of initial dicyanate in Table 4	Ultimate strength, kgf cm^{-2}					
	−55°	24°	82°	121°	149°	177°
1	308	308	273	210	—	95
2	280	280	245	245	140	70
3	385	266	245	203	140	84
8	112	126	98	126	—	91

Table 4. The structures and melting points of oligoarylene oxide dicyanates.

No.	Dicyanate	M.p., °C
1		133–135
2		110–115
3		98–100
4		120
5		100
6		100
7		139–140
8		70
9		120

The synthesis of the dicyanates of oligoaryleneoligosulphones[86] and the oligoarylates[87] and polycyanates based on them[88] has been achieved recently. In contrast to earlier patents[84,85], in this case the initial oligoaryleneoligosulphones with terminal hydroxy-groups were obtained by the condensation of the dihalogeno-derivatives of diphenyl sulphone with alkoxides derived from 2,2-di-(4-hydroxyphenyl)propane in dimethyl sulphoxide[86]:

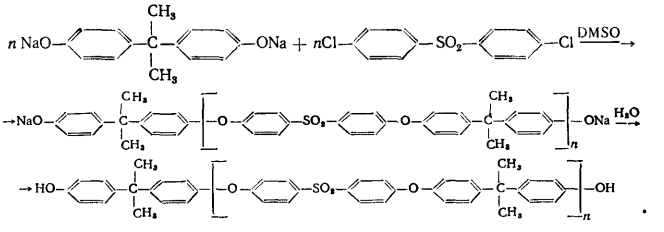
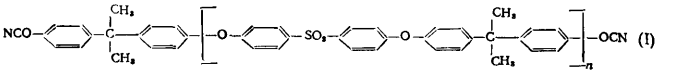
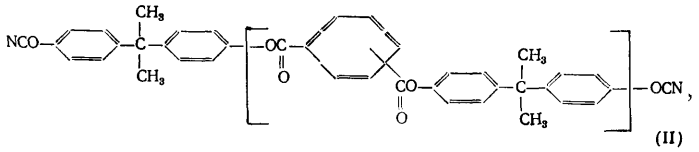


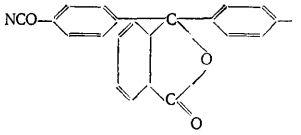
Table 6 presents certain thermal characteristics of a number of polycyanates based on the dicyanate esters of oligoaryleneoligosulphones:

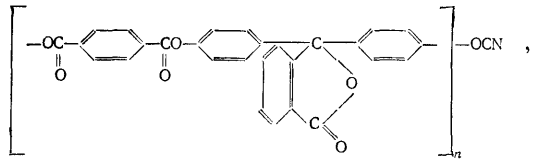


and oligoarylates:

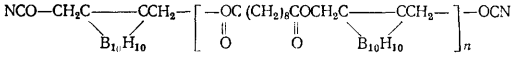


(II)





(III)



(IV)

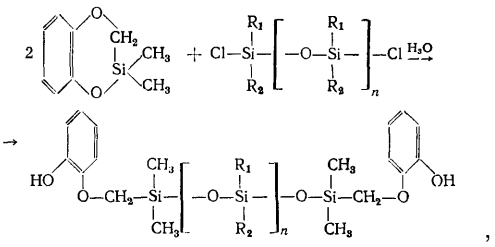
Table 6. Thermal characteristics of network polymers based on the oligomeric dicyanates (I), (II), (III), and (IV).

n	$T_{w.l.}$, °C		T (5%), °C*		T (10%), °C*		$T_{o.d.}$, °C
	in air	in argon	in air	in argon	in air	in argon	
Polymers based on oligodicyanates (I)							
1	360	370	400	380	415	400	240
3	380	—	420	—	435	—	220
5	400	390	440	410	450	420	190
10	405	—	435	—	460	—	190
Polymers based on oligodicyanates (II)							
1	345	350	390	365	410	380	220
3	330	—	380	—	400	—	210
5	340	350	390	375	425	390	190
Polymers based on oligodicyanate (III)							
5	350	—	390	—	400	—	290
Polymers based on oligodicyanate (IV)							
7	300	—	345	—	380	—	10

*Temperatures at which the polymer loses 5 and 10% of its weight respectively.

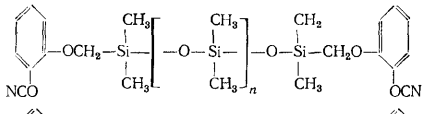
The study of the influence of the degree of cross-linking on the heat resistance of these polymers showed that, with increase of the degree of cross-linking, the glass temperatures of the polymers increase relative to linear high-molecular-weight polymers with a similar structure. Furthermore, in contrast to high-molecular-weight linear analogues, the thermomechanical curves for polycyanates show a viscoelastic plateau, the upper temperature limit of which is between 300° and 350°C, depending on the structure of the initial oligomer[88]. The region of the viscoelastic state of a carborane-containing oligoester was found to lie in the temperature range from 10° to 350°C, i.e. the polymer is an elastomer at room temperature.

Oligomeric dicyanates and oligodimethyl- and methylphenyl-siloxanes have also been used as the starting compounds for the synthesis of polycyanates[88-95]. The initial bisphenols for the synthesis of these dicyanates were obtained[88,89,93,94] by the cohydrolysis of $\alpha\omega$-dichlorosiloxanes with 2,2-dimethylbenzo-2-sila-1,4-dioxan via the following mechanism:

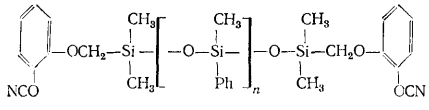


where n = 1 - 150 for $R_1 = R_2 = CH_3$, n = 1–20 for R_1 = CH_2 and $R_2 = C_6H_5$, and n = 1–10 for $R_1 = R_2 = C_6H_5$.

Dicyanate esters based on these bisphenols were synthesised by acylating them with halogenocyanogens in the presence of tertiary amines[88,90]. Two types of oligomeric organosilicon dicyanates were obtained:



(V)



(VI)

Certain properties of the polymers based on these compounds are listed in Table 7.

Table 7. Properties of organosilicon polycyanates[88,89] based on the oligomeric dicyanates (V) and (VI).

n	Glass point, °C	$T_{w.l.}$, °C	
		in air	in argon
Polymers based on oligodicyanates (V)			
0	180	250	260
1	14	260	—
5	−70	290	300
10	−75	300	—
25	−80	315	325
50	−100	330	—
70	−100	340	—
100	−120	360	300
Polymers based on oligodicyanates (VI)			
3	−10	285	—
5	−20	300	—
10	−25	300	—

Depending on the length of the siloxane chain between the nodes of the network, these polymers have glass points between −120° and 180°C. It has been shown that organosilicon polycyanates have a high thermal stability and the region of their viscoelastic state lies within a wide temperature range: from −120° to 340°C, i.e. up to the temperatures of the onset of their degradation[88,91,95].

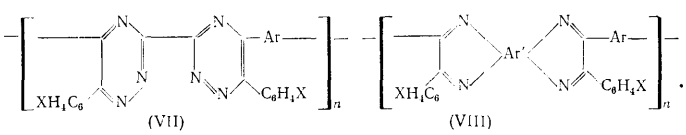
There are also patent data for cross-linked plastics obtained by the polycyclotrimerisation of the terminal N≡C–O groups of a prepolymer synthesised from the product of the reaction of ϵ-caprolactone with various bisphenols[96]. These polymers have a high strength and hardness, exhibit strong adhesion, and can be used as coatings, binders, insulators, etc. The formation of

phenol-formaldehyde resins containing cyanate groups, by treating a novolak resin with chlorocyanogen in the presence of tertiary amines, has been described[97,98]. The polymers, hardened at elevated temperatures, are recommended as plastics, adhesives, and coatings.

3. Polymers with Cyanate Side Groups

Studies devoted to the modification of known polymers by the introduction into their structure of reactive cyanate groups have been published[99-102]. Subsequent cyclotrimerisation of these groups or their interaction with various compounds yields cross-linked systems, which makes it possible to impart many new valuable properties to the initial polymers.

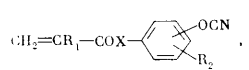
Thus Hergenrother[99] obtained high-molecular-weight polyphenylene-*asym*-triazines having the general formula (VII), where Ar = *m*- or *p*-C_6H_4 or *p*-$C_6H_4OC_6H_4$ and X = H, C_2H_5, OCH_3, OC_6H_5, C_6H_5, OH, Br, CN, OCN, OC_6H_4CN, and polyphenylenequinoxalines having the general formula (XIII), where Ar and X are the same as above (X can be in addition CH_3) and Ar′ = $C_6H_3C_6H_3$ or $C_6H_3COC_6H_3$.



(VII) (VIII)

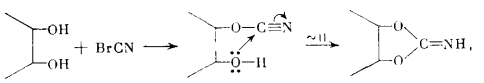
It has been shown that heat treatment of polymers with cyanate groups entails their cross-linking as a result of the cyclotrimerisation of the groups, which leads to a raising of the glass points of the resulting polymers compared with the initial polymers.

A method for the synthesis of cyanates from polymers containing vinyl groups and having the general formula



where R_1 = H, CH_3, or Cl, R_2 = H, Alk(C_{1-4}), or Cl and X = O or H, has been described[100]. The above cyanates have been homopolymerised or copolymerised via the vinyl group with butadiene, isoprene, various acrylates, styrene, α-methylstyrene, and other compounds. Linear polymers were obtained with different contents of cyanate side groups. These polymers, which were subsequently heat-treated at 70–200°C, were converted into cross-linked systems as a result of the cyclotrimerisation of N≡C–O groups[100].

A method has been patented for the synthesis of polymers with cyanate groups, which were subsequently used to bind organic compounds containing a primary or secondary amino-group or an OH group[101]. For this purpose, a polymer containing primary or secondary OH groups (for example cellulose, agar, etc.) is treated with cyanate esters having the general formula $R(OCN)_X$ (R = halogenoalkyl and substituted or unsubstituted aromatic or heterocyclic groups and *x* = 1 or 2). Such a cyanate-activated polymer is capable of binding aminoacids and other compounds. The mechanism of the interaction of mercerised cellulose with bromocyanogen has been investigated[102] and it has been established that this results in the formation of cellulose iminocarbonate via the mechanism



the product being capable of interacting with protein. Such cellulose treated with BrCN has been used successfully as a matrix for the binding of biologically active proteins and their insolubilisation.

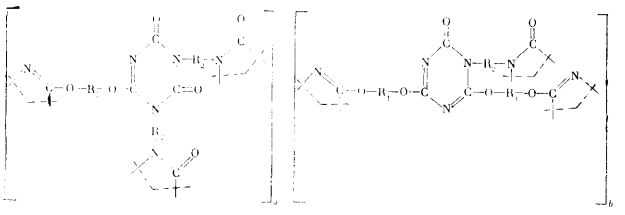
4. Copolymers of Cyanate Esters

The modification of the properties of polycyanates in the desired manner can be achieved by the copolymerisation of dicyanates with one another, with monocyanates, and with various compounds to form network structures and also non-cross-linked soluble polymers.

An advantage of the copolymerisation of dicyanates with one another is that the mixtures of monomers are converted into a melt at lower temperatures than the initial dicyanates during their homopolymerisation and do not crystallise from the melt on cooling, which greatly simplifies the technology of the processing of such polymers[103]. Furthermore, by varying the structure and proportions of the initial dicyanates, it is possible to alter specifically properties of the polycyanates such as heat resistance, thermal stability, and physicomechanical parameters[82,103,104].

The copolymerisation of aryl dicyanates with monocyanate can yield, depending on the ratio of the initial monomers, polycyanates with different degrees of cross-linking as well as fusible and soluble polymers[82,104]. However, the physicomechanical properties of such copolymers are greatly inferior to those of the homopolymers of dicyanates and are sharply impaired with decrease of the degree of cross-linking. This is probably associated with the breakdown of the regularity of the cross-linking occurring in the homopolymerisation of dicyanates, so that cross-linked copolymers of aryl dicyanates with monocyanate become analogous to randomly cross-linked rigid-chain polymers (epoxide and phenol-formaldehyde polymers, polymers of the polyphenylene type, etc.) as regards physicomechanical properties[103]. Furthermore, the breakdown of the regularity of the cross-linking by the introduction of monocyanate into the polymers leads to a decrease of their heat resistance and thermal stability compared with homopolymers[103].

The synthesis of copolymers of isocyanates with cyanates having the general formula



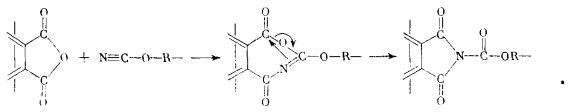
has also been described[105]. Here R_1 and R_2 are aromatic mono-, bi-, or poly-cyclic groups containing the H, N≡C–O, CH_3, F, Cl, Br, N=C=O, NH_2, or OH ring substituents. Bicyclic groups can be separated by $-CH_2-$, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-O-$, $-SO_2-$,



bridges, siloxane fragments, and aliphatic, cyclic aliphatic, arylalkyl, and fluorine- or boron-containing groups.

The resulting copolymers of isocyanates with cyanates have effective temperature characteristics and satisfactory physicomechanical parameters. They can be used as thermostable compositions, coatings, varnishes, binders for glass-fibre-reinforced plastics, etc.[105] Thus the copolymer of 9,9-di-(4-cyanatophenyl)fluorene and 9,9-di-(4-isocyanatophenyl)fluorene begins to decompose in air (according to thermogravimetric data) at 440°C and the temperature of the onset of deformation is 480°C.

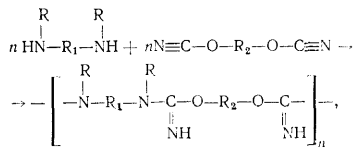
The interaction of acid anhydrides with cyanate esters, leading to the formation of imidocarbonates, was described in 1970:[106]



This interesting reaction of cyanate esters was used to synthesise a new type of polymer—polyimidocarbonates[107-109]. These polymers were obtained by the migration copolymerisation of various dianhydrides of tetracarboxylic acids and aryl dicyanates in the melts or in solution in a high-boiling organic solvent. Depending on the structure of the initial compounds, the polymers had a softening temperature in the range 230–260°C, the temperature of the onset of their decomposition in air was in the range 300–350°C, and μ_{int} in DMF was up to 0.5 dl g^{-1}. In order to determine the structures of the polymers obtained, the authors[108,109] synthesised compounds simulating the main chain of polyimidocarbamates, namely *N*-(phenoxycarbonyl)phthalimide, di-*NN'*-(phenoxycarbonyl)pyromellitimide, and 4,4'-di-(*N*-phthalimidacarbamatophenyl)-2,2-propane.

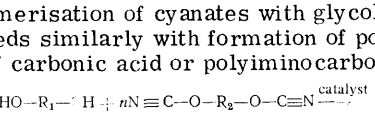
Certain characteristics of the formation of polyimidocarbamates were investigated in relation to the interaction of 2,2-di-(4-cyanatophenyl)propane and the dianhydride of pyromellitic acid[109]. It was found that, for an equimolar reactant ratio, the product is a linear, fusible, and soluble polyimidocarbamate. With increase of the content of cyanate groups in the initial mixture and also when polyfunctional esters or acid anhydrides with a functionality > 2 are used, the products are cross-linked, infusible, and insoluble polymers[107]. The synthesis of a number of linear polymers based on bifunctional cyanates has been described[72,110,111].

It is also known that cyanate esters readily interact with primary and secondary amines, forming isourea ethers[25,29,30]. The migration copolymerisation of primary and secondary diamines with dicyanates yielded polymeric isourea ethers or polyisoureas[110,111] via the mechanism:



where R_1 is an aliphatic, alicyclic, arylalkyl, aryl, or heterocyclic group, R = H, alkyl, or aryl, and R_2 = aryl, alkyl, or a heterocycle. When cyanates or amines with a functionality > 2 are used, the products are cross-linked polymers[110,111].

The copolymerisation of cyanates with glycols and bisphenols proceeds similarly with formation of polymeric iminoesters of carbonic acid or polyiminocarbonates[72]:



However, in contrast to the synthesis of polyisoureas, the formation of polyiminocarbonates proceeds in the presence of bases such as alkali metal alkoxides, hydroxides, carbonates, metal hydrides, tertiary amines, etc.[72]

Departure from equimolar ratios in the case of bifunctional starting materials leads to the formation of polymers with terminal cyanato- or hydroxy-groups[72].

IV. THE SPECIFIC FEATURES OF THE PROPERTIES AND STRUCTURES OF POLYCYANATES

Polycyanates are a new class of polymers with a regular network structure. Aromatic polymers having this type of structure with a high degree of cross linking were previously unknown. The change from the previously known randomly cross-linked structures to structures with a regularly constructed network, as in polycyanates, should have led to a quantitative change in many properties of the polymers. Indeed a number of unusual properties drew attention already in the first studies on polycyanates. Subsequently these polymers were investigated in greater detail and new properties, unusual for cross-linked polymeric systems, were found.

The results of studies devoted to a detailed investigation of thermal, physicomechanical, and other properties of polycyanates as well as the structural parameters of these polymers are discussed below. Particular attention has been devoted to the specific features of polycyanates due to their regularly cross-linked structure.

The majority of polytriazines, to the class of which polycyanates belong, are known to exhibit an enhanced thermal stability[45,47,55,112-115] due to the aromatic nature of the triazine ring whose thermal stability is close to that of the benzene ring[55,115-118]. A number of studies on the influence of the chemical structure of the initial monomers on the thermal stability of the polycyanates have been described in the literature[55,115,119,120]. Furthermore, in the majority of papers on the synthesis and properties of these polymers, certain characteristics of their thermal stability are also quoted. Investigations of the thermal stability of polymers having this type of structure but obtained by the polycondensation or polymerisation of monomers containing an existing *s*-triazine ring are also of definite interest[47,121,122].

Table 8. Results of the thermogravimetric analysis of polycyanates on heating in air (at a rate of 4.5 K min^{-1}).

Polycyanate	Initial aryl dicyanate	Decrease in weight of polymers, %						
		300°	350°	400°	450°	500°	550°	600°
PTs-19	NCO—C_6H_4—CH_2—C_6H_4—OCN	—	1	3	19	27	56	73
PTs-1	NCO—C_6H_4—$C(CH_3)_2$—C_6H_4—OCN	—	2	9	42	51	65	93
PTs-15	NCOC_6H_4—$C(CF_3)_2$—C_6H_4OCN	1	2	5	17	27	58	82
PTs-17	NCOC_6H_6—C(H)(C_6H_5)—C_6H_4OCN	—	—	2	20	31	46	78
PTs-34	NCOC_6H_4—$C(CH_3)$(C_6H_5)—C_6H_4OCN	1	4	16	41	52	75	95
PTs-23	NCOC_6H_4—$C(C_6H_5)_2$—C_6H_4OCN	—	—	6	26	32	45	70
PTs-2	3,3-di-(4-cyanatophenyl)phthalide	—	1—2	2	20	33	50	80
PTs-9	9,9-di-(4-cyanatophenyl)fluorene	—	—	—	17	22	38	72
PTs-10	9,9-di-(4-cyanatophenyl)-10-anthrone	—	2	6	19	28	50	79
PTs-1V	1,2-di-(4-cyanatophenyl)carborane	—	—	—	10	4	0	4.5**
PTs-R	*m*-NCO—C_6H_4—OCN	—	1	11	23	31	46	71
PTs-G	*p*-NCO—C_6H_4—OCN	—	5	17	36	45	58	92
PTs-4	*p,p'*-NCO—C_6H_4—C_6H_4—OCN	—	5	18	27	37	67	96

*The designations of the polycyanates here and in Tables 9 and 10 are the same as in the original papers[54,64,115,119,120].

**In contrast to other polymers, the carborane-containing polycyanate shows a 4.5% increase in weight at 600°C in air.

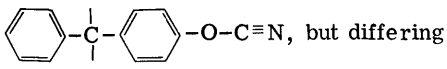
A comparative study has been made of the thermal and thermo-oxidative degradation under dynamic and isothermal conditions of polycyanates obtained by the polycyclotrimerisation of aryl dicyanates having the general structure , but differing in the substituents at the central carbon atom [119]. The data obtained by the authors are presented in Tables 8–10.

Table 9. Results of the thermogravimetric analysis of polycyanates on heating in helium.

Polycyanate	Decrease in weight of polymers, %							
	350°	400°	450°	500°	550°	600°	700°	900°
PTs-19	2	7	25	31	38	46	40	55
PTs-1	4	9	25	37	53	57	60	65
PTs-15	3	8	25	31	54	61	65	68
PTs-17	4	12	17	29	40	50	54	57
PTs-34	—	1	12	21	31	37	40	43
PTs-23	—	1	7	13	20	28	32	33
PTs-2	1	3	12	22	33	39	43	46
PTs-9	—	1	6	13	17	24	28	31
PTs-10	1	5	17	23	31	35	39	42
PTs-1V	2	7	12	14	14	14	15	16
PTs-R	4	10	28	34	38	42	48	57
PTs-G	1	5	22	36	41	45	51	59
PTs-4	3	9	22	27	31	34	40	47

Table 10. Results of the thermogravimetric analysis of polycyanates under isothermal conditions.

Polycyanate	Decrease in weight of polymers, %*					
	5 min	10 min	20 min	30 min	40 min	60 min
PTs-19	1/5	2/8	3/12	4/15	4/17	4/20
PTs-1	2/23	4/31	7/42	8/49	9/54	10/58
PTs-15	4/7	4/ 8	5/12	5/13	5/13	5/14
PTs-17	11/63	15/69	18/73	19/75	20/75	20/77
PTs-34	2/3	2/6	2/10	2/12	2/15	2/18
PTs-23	3/7	4/9	4/10	5/11	5/12	5/14
PTs-2	2/4	2/6	2/8	2/8	2/8	2/9
PTs-9	2/3	2/4	2/5	2/6	2/6	2/6
PTs-10	2/3	3/4	3/5	3/5	3/5	3/6
PTs-1V	0/0	0/0	0/1	0/1	0/1	0/1
PTs-R	3/7	5/10	7/13	9/16	8/17	8/18
PTs-G	2/—	4/—	5/—	5/—	5/—	5/—
PTs-4	1/3	2/6	3/8	4/9	4/10	4/10

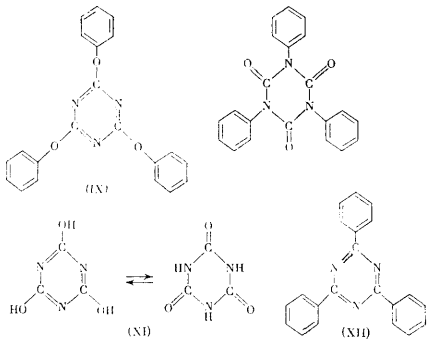
*Number on the left—at 300°C, number on the right—at 350°C.

It was found that the decomposition reaction of polycyanates with different structures in air is of the same type; it proceeds in several stages and is accompanied by the evolution of heat. This is indicated by the exothermic effects observed in the temperature ranges 380–420° and 490–580°C. In the first decomposition stage, the decrease in weight is 20–40% and in the second stage up to 90%. An exception is the thermo-oxidative degradation of the polycyanate based on dicyanatodiphenylcarborane. The beginning of the decrease in the weight of this polymer is observed at 390°C and at 450°C the weight loss is 10%. On further increase of temperature, the weight of the polymer rises and at 650°C is 107% of the initial value. The weight then again gradually decreases, amounting to approximately 96% of the initial value at 850°C (Table 8). Other carborane-containing polycyanates behave similarly [72,75,77,79].

In an inert atmosphere, the decomposition of polycyanates also proceeds in two stages. Under these conditions the temperatures of the onset of decrease in weight and the temperature ranges corresponding to the vigorous decomposition of polycyanates are somewhat displaced towards higher temperatures compared with degradation in air [55,119]. Large residues of carbon are characteristic of the degradation of polycyanates in an inert atmosphere up to 900°C [55, 119].

In the series of polycyanates based on aryl dicyanates with different substituents at the central carbon atom, polymers with polycyclic groups (phthalide, fluorene, or anthrone types) at the central carbon atom in the initial dicyanate have a high thermal stability [55,119].

In order to investigate further the processes occurring following the exposure of polycyanates to elevated temperatures, a study was made of the kinetics of the decomposition of polycyanates based on 2,2-di-(4-cyanatophenyl)-propane (PTs-1), 4,4′-dicyanatobiphenyl (PTs-4), and 9,9-di-(4-cyanatophenyl)fluorene (PTs-9), as well as the degradation of the model compounds diphenyl cyanurate (IX), triphenyl isocyanurate (X), cyanuric acid (XI), and triphenyl-*s*-triazine (XII) [115,120]:



(IX) (X) (XI) (XII)

A study of the degradation process in air and *in vacuo* showed that the decomposition of polycyanates proceeds as a first-order reaction and obeys the Arrhenius equation. A comparative study of the kinetics of the decomposition of the polymers PTs-1, PTs-4, and PTs-9 *in vacuo* and in air showed that the polycyanate based on 9,9-di-(4-cyanatophenyl)fluorene, containing bulky subgroups, is more resistant to the action of high temperatures than the other two polymers. It was established that the presence of moisture in the polymers has a significant influence on the nature and degree of their decomposition.

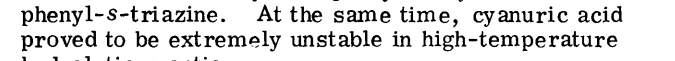
The study of the degradation products of polycyanates showed that they consist mainly of CO_2, CO, H_2, compounds containing the triazine ring (cyanuric acid and its phenyl esters), phenol, and bisphenols. Furthermore, benzene, biphenyl (in the degradation of the polycyanate PTs-4) and fluorene (in the degradation of the polycyanate PTs-9) were detected in the degradation products.

Since the polycyanates investigated are highly structured complex systems, a detailed investigation of the degradation of which presents certain difficulties, a study was made of the degradation of triphenyl cyanurate, a compound which simulates the principal bonds in the three-dimensional structure of the polymer, to elucidate the mechanism of the decomposition process [55,115]. The results of the study of the degradation of this compound by chromatographic and mass-spectrometric methods showed that, as in the degradation of the polymers PTs-1, PTs-4, and PTs-9, the principal decomposition products are carbon oxide, phenol, and cyanuric acid. Comparison of the

thermal stabilities of the above model compounds derived from triazine permitted the conclusion that triphenyl-*s*-triazine exhibits the highest thermal stability (CO, CO_2, and H_2 were not detected in the volatile degradation products up to 500°C)[115]. The presence of water at high temperatures has virtually no influence on the temperature limits of the stability of triphenyl isocyanurate and triphenyl-*s*-triazine. At the same time, cyanuric acid proved to be extremely unstable in high-temperature hydrolytic reactions.

The study of the decomposition products of polycyanates and their model compounds led to a degradation mechanism involving heterolytic and homolytic decomposition reactions[115]. It has been suggested that the degradation of polycyanates begins with the hydrolytic cleavage of the ester linkage and is accompanied by the subsequent decomposition of the triazine ring via both heterolytic and homolytic mechanisms. It has been noted that the effect of the hydrolysis of the ester linkage in the early stages may be somewhat suppressed by the introduction of bulky side groups into the polycyanate chain[115].

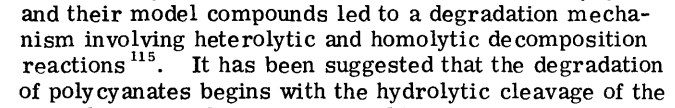
The influence of molecular weight (M_C) and of the chemical nature of the internodal fragments of polycyanates on their thermal and thermo-oxidative degradation has also been investigated[88]. In the polymers chosen for investigation, the internodal fragments were oligoarylene-oligosulphones:



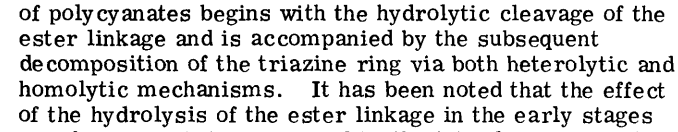
$$-OC_6H_4C(CH_3)_2C_6H_4-[-OC_6H_4SO_2C_6H_4OC_6H_4C(CH_3)_2C_6H_4-]_n-O-,$$

$$n=1, 3, 5, 10,$$

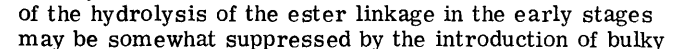
oligoarylates:



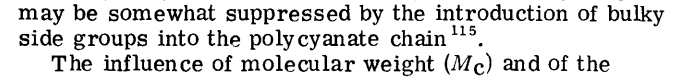
$$-OC_6H_4C(CH_3)_2C_6H_4-[-OCOC_6H_4COOC_6H_4(CH_3)_2C_6H_4-]_n-O-,\ n=1,3,5 \text{ and}$$



$$-OC_6H_4-\underset{\underset{O}{\diagup\diagdown}}{C}-C_6H_4-[-OCOC_6H_4COOC_6H_4-\underset{\underset{O}{\diagup\diagdown}}{C}-C_6H_4-]_n-O-,\ n=5,$$

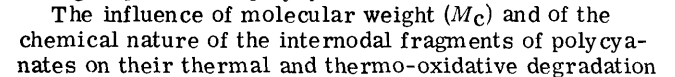


a carborane-containing oligoester:



$$-OCH_2-C(B_{10}H_{10})-CH_2-[-OCO(CH_2)_8COOCH_2-C(B_{10}H_{10})-CH_2-]_n-O-,\ n=7,$$

and oligosiloxanes:



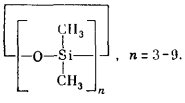
where n = 3, 5, or 10 for $R_1 = CH_3$ and $R_2 = C_6H_5$ and n = 0, 1, 5, 10, 25, 50, 70, or 100 for $R_1 = R_2 = CH_3$.

It was found that polycyanates based on oligoarylene-oligosulphones exhibit the highest thermal and thermo-oxidative stability (Table 6). An increase of M_C of these polymers entails some increase in thermal stability. When oligoarylates are used as the internodal fragments, M_C has hardly any influence on the temperature of the onset of decrease in their weight in air and in an inert atmosphere[88]. CH_4, H_2, and CO_2 were detected in the gaseous decomposition products of polycyanates with oligoarylene-oligosulphone internodal fragments, while in those with oligoarylate fragments CO was also detected.

The carborane-containing polymer has a lower temperature of the onset of decomposition in air compared with polycyanates containing oligoarylene-oligosulphone and oligoarylate internodal fragments, but, as for other carborane-containing polycyanates[73,75,77,79], it is characterised by a higher coke content at 900°C, while aromatic polymers are combusted almost entirely in air at 900°C.

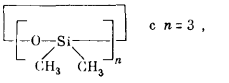
A study of the degradation of polycyanates containing oligosiloxane fragments of different lengths between the network nodes showed that an increase of M_C entails an increase of the thermal and thermo-oxidative stabilities of the polymers, but, starting with a specific value of M_C, the thermal stability remains constant or actually diminishes somewhat.

The nature of the degradation of silicon-containing polycyanates, particularly at elevated temperatures, is the opposite of that of aromatic polycyanates, which are combusted almost in their entirety in air but leave appreciable carbon residues in an inert atmosphere at temperatures in the range 700–900°C. Appreciable coke residues, increasing with increase of M_C, are observed in the thermo-oxidative degradation of organosilicon polymers at high (up to 900°C) temperatures. On the other hand, siloxane-containing polycyanates decompose almost entirely on degradation in argon and for high values of M_C the coke residues are insignificant. These findings have been explained[88] by the fact that, in the presence of oxygen, the siloxane chains form a structure via the organic groups attached to silicon, while in an inert atmosphere they are depolymerised with liberation of low-molecular-weight products having the structure



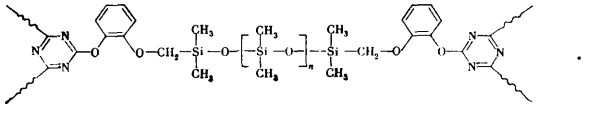
$$\left[-O-Si(CH_3)_2-\right]_n,\ n=3\text{-}9.$$

H_2, CH_4, and CO_2 were detected in the gaseous degradation products of silicon-containing polycyanates, while 2,2-dimethylbenzo-2-sila-1,4-dioxan (DMBD), catechol, the cyclic siloxane

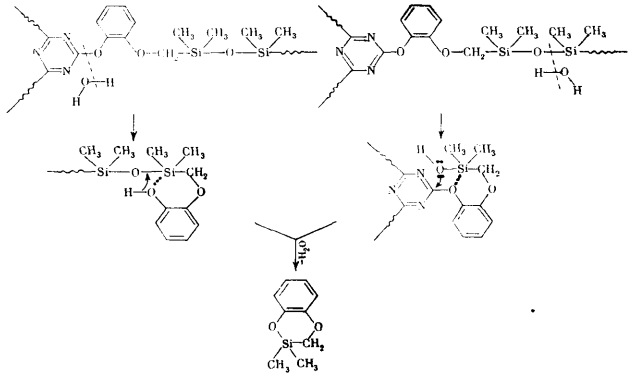


$$\left[-O-Si(CH_3)_2-\right]_n,\ n=3,$$

with n = 3 (D_3) and n = 4 (D_4), and other compounds were found among the low-molecular-weight substances[88]. Table 11 presents data obtained by pyrolytic gas chromatography for the composition of the low-molecular-weight products of the degradation of organosilicon polycyanates with the following structure of the internodal fragment:



A possible mechanism for the degradation of organosilicon polycyanates has been suggested on the basis of data obtained in the study of this process[88]. Thus the formation of 2,2-dimethylbenzo-2-sila-1,4-dioxan (Table 11), detected in considerable amounts in the degradation products, can proceed via the mechanism:



Interesting data have been obtained in a study[123] of the influence of the structure of the initial dicyanate esters, in particular the nature of the substituents at the central carbon atom of aryl dicyanates, on the physical characteristics of the polymers based on them. The results obtained in this and a number of other investigations[54,55,73-77,80,124-126] are presented in Table 12.

Table 11. The compositions of the degradation* products of polycyanates with oligodimethylsiloxane internodal fragments.

n**	Degradation temp., °C	Amount of evolved products, mole/mole of structural unit					
		DMBD	catechol	D_3	D_4	D_5	D_{7-9}
0	300	1.680	0.430	0.220	0.070	0.020	0.005
0	350	2.035	0.520	0.220	0.110	0.015	0.010
0	450	0.895	0.128	0.270	0.130	0.020	0.015
0	550	0.437	0.028	0.320	0.130	0.015	0.020
5	300	2.450	0.270	0.240	0.090	0.030	0.010
5	350	1.930	0.215	0.270	0.140	0.030	0.015
5	450	0.650	—	0.770	0.290	0.050	0.040
5	550	0.535	—	1.550	0.710	0.130	0.110
100	300	—	—	16.200	12.400	1.290	0.290
100	450	—	—	26.500	20.000	2.670	0.540
100	550	—	—	20.000	35.500	6.420	0.960

*The specimens were maintained at a specified temperature for 15 min.

**n is the number of repeating groups $-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-$ in the internodal fragment.

Table 12. Physical properties of polycyanates.

No.	Impact strength, kgf cm cm^{-2}	Ultimate bending strength × 10^{-3}, kgf cm^{-2}	Brinel hardness × 10^{-3}, kgf cm^{-2}	Density at 20°C, g cm^{-3}	Packing coefficient	Result of X-ray diffraction analysis **	References
1	18	1.92	1.40	1.414	0.688	a.(cr.)	54,55,123
2	12	1.73	1.50	1.431	0.697	cr.(1.ord.)	54,55,123
7	6	1.47	1.60	1.319	0.689	cr.(m.ord.)	54,123
9	20	1.60	1.35	—	—	a.	54
10	23	1.22	1.10	1.307	0.688	cr.(m.ord.)	54,55,123
13	18	1.80	1.25	—	—	a.	54
14	30	1.40	1.20	1.235	0.686	a.(cr.)	54,55,123
16	24	1.46	1.25	1.528	0.682	a.	54,55,123
17	10	1.59	1.35	1.255	0.689	»	54,55,123
18	17	1.85	1.46	1.229	0.684	»	54,55,123
19	5	1.62	1.63	1.220	0.681	»	54,55,123
20	6	2.02	1.65	1.322	0.673	»	54,55,123
21	5	1.54	1.70	1.269	0.688	»	54,55,123
22	6	1.69	1.60	1.288	0.685	cr.(1.ord.)	54,55,123
28	8	1.85	1.70	—	—	a.	73
29	30	1.30	1.60	—	—	»	74,75
30	17	1.50	1.40	—	—	»	77
31	15	1.40	1.30	—	—	»	79
32	14	1.20	1.40	—	—	»	79
33	20	—	—	—	—	»	80
34	30	—	—	—	—	»	80

*The numbers of the polymers correspond to those in Table 2.

**a. amorphous, a.(cr.) amorphous with signs of crystallinity, cr.(1.ord.) crystalline with a low degree of order, and cr.(m.ord.) crystalline with a moderate degree of order.

The most striking feature of the study of a systematic series of polycyanates[54,55,123] based on bicyclic aromatic dicyanates (see Nos. 7–29, Table 12), differing in the nature of the bridge group between the phenyl groups, is that the polymers obtained from dicyanates having a flexible bridge group and small substituents at the central carbon atom (polymers Nos. 9–16, Table 12) have anomalously high specific impact strengths (up to 30 kgf cm cm^{-2} in contrast to all known cross-linked aromatic polymers[127] On the other hand, the presence at the central carbon atom of identical and aromatic substituents (polymers Nos. 17–19) and also of polycyclic groups (polymers Nos. 20–28) leads to an appreciable decrease of this parameter in cast polycyanate specimens. However, in the latter instances the bending strength of the polycyanate is somewhat enhanced[54,55,103,123]. This type of influence of the structure of the substituents at the central carbon atom in bifunctional derivatives was also observed previously for a series of heterochain linear polymers[128-131].

The decrease of the distance between the network nodes to a single phenylene group (polycyanates derived from 1,3- and 1,4-dicyanatobenzenes) leads to an appreciable increase of the specific impact and bending strengths of the cast polymer specimens[123]. Furthermore, block specimens of aromatic and a number of organoelement polycyanates have high bending strengths, a Brinell hardness of approximately 1000–1700 kgf cm^{-2}, a tensile strength in excess of 1000 kgf cm^{-2}, a modulus of elasticity of approximately 30 000–50 000 kgf cm^{-2}, and a relative elongation on extension of 3–6%.[54,55,73-77,80,123,126] These polymers retain effective physicochemical properties also at elevated temperatures, as can be seen from Table 13 for the polycyanate based on 2,2-di-(4-cyanatophenyl)propane.

Table 13. Physicomechanical properties of the polycyanate based on 2,2-di-(4-cyanatophenyl)propane at different temperatures.

Temp., °C	Tensile strength, kgf cm^{-2}	Relative elongation, %	Modulus of elasticity, kgf cm^{-2}
20	1100	4.5	32 000
200	650	5.6	22 000
250	500	6.1	17 000

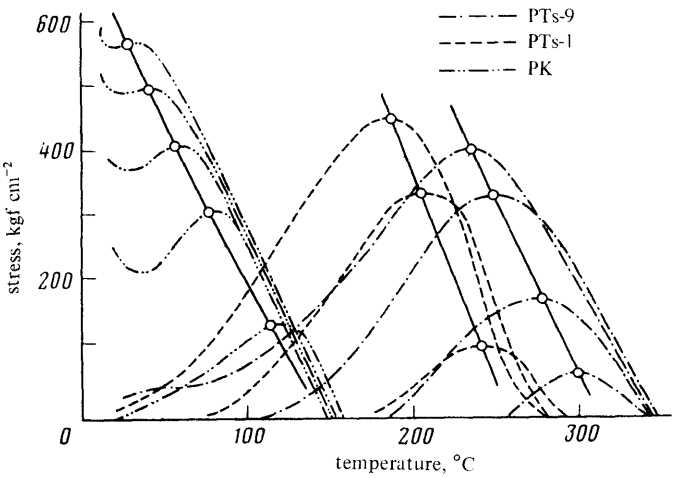
In order to elucidate the causes of the unusual mechanical properties of polycyanates, a study was made of the formation of the supermolecular structures of these polymers at different stages of their synthesis, starting from the initial monomer [2,2-di-(4-cyanatophenyl)propane] and continuing as far as the regular network system, with virtually quantitative conversion of the functional groups[64]. It was found that material with a globular structure is formed initially in polycycloprimerisation against the background of the characteristic cryptocrystalline structure of the monomer[64]. The size of the globules does not remain constant during polymerisation but gradually diminishes from approximately 500 to 100–200 Å. Subsequently the globules were found to aggregate in the final stage of polymerisation (for the conversion of the N≡C–O groups of approximately 98%) into fibrille-like formations.

Simultaneously with the study of the supermolecular structure of the polycyanates, the relaxation properties of the solid networks at different stages of the conversion of the N≡C–O groups of the initial monomer were also investigated[64]. With an increase of the degree of conversion, the relaxation curves are initially displaced towards highe

stresses and, after the attainment of approximately 90% conversion of the monomer, begin to shift to the region of lower stresses. The parameters of the Kohlrausch equation were calculated for various stages of the process. The results show that, as the polycyclotrimerisation of aryl dicyanates proceeds and with the consequent increase of the regularity of the network formed, the nature of the supermolecular structure of the polymer alters, which leads in its turn to a steady change of the mechanical properties of the network system–to an increase of elasticity[64].

It may be that, in the usual thermoreactive systems, the formation of a regular defect-free network can also lead to polymeric materials with an enhanced resistance to impact stresses and with an improved elasticity.

The study of the thermomechanical properties[53] of polycyanates showed that the temperatures of the onset of their deformation lie in a comparatively narrow range (360–410°C). However, the nature of the thermomechanical curves for polycyanates suggests that the deformation temperature is related to the degradative processes occurring in the polymers. This is confirmed by the fact that the temperatures of the onset of decomposition of polycyanates in air (from thermogravimetric data) lie in this region.



The regions corresponding to the effectiveness of the polycarbonate based on 2,2-di-(4-hydroxyphenyl)propane (PC) and the polycyanates based on 2,2-di-(4-cyanatophenyl)-propane (PTs-1) and 9,9-di-(4-cyanatophenyl)fluorene (PTs-9).

For a more detailed comparison of the heat resistances of highly cross-linked polycyanates synthesised from the dicyanate esters of bisphenols of different structures, the regions where the polymers can be used effectively were determined over a wide range of temperatures and mechanical stresses (see Figure).[123] The similarity of the non-isothermal stress relaxation curves and the curves bounding the region where the polymer is efficient, obtained for highly cross-linked systems (polycyanates) and for the linear heterochain polymers investigated in detail in previous studies[128–132], is striking; the Figure presents the polycarbonate curve as an example. The replacement of the isopropylene group by the fluorene group leads to an increase of the heat resistance of polycyanates over the entire range of temperatures and stresses investigated.

A study was also made of the influence of a number of other features of the structure of the initial dicyanate esters on the parameters of the region of the effective use of the polycyanates based on them[123]. It has been shown for polycyanates based on the oligomeric dimethylsiloxane dicyanates (V) that M_C has a significant influence on many physicomechanical parameters of these polymers[88,91,95]. With decrease of M_C, an increase of tensile strength (σ_t) and the modulus of elasticity (E_t) as well as a decrease of the relative elongation on extension (ϵ_t) are observed (Table 14).

Table 14. The influence of M_C on the physicomechanical properties of organosilicon polycyanates based on the oligodicyanates (V).

Number of dimethylsiloxane groups in internodal fragment	σ_t, kgf cm^{-2}	ϵ_t, %	E_t, kgf cm^{-2}
1	25	12	208
5	4	40	10
25	2	50	3
50	1	90	1
70	1	120	1

The packing coefficients for monolithic specimens of many amorphous and weakly crystalline linear polymers, having a large variety of structures and obtained by both polymerisation and polycondensation, vary within extremely narrow limits[133] and their packing densities are approximately the same (k_{av} = 0.681). The packing coefficients have also been recently calculated for sterically structured systems[123]; these parameters for a number of polycyanates are listed in Table 12.

It has been found that the packing coefficients for closely cross-linked polymers with a wide variety of structures lie within a narrow range (0.673–0.697), the average value of the parameter for the polycyanates (0.686) being close to the average value for linear polymers (0.681). The virtual identity of the packing coefficients for linear and cross-linked polymers shows that the amorphous and weakly crystalline sterically structured, infusible, and insoluble polymers are just as closely packed as the linear, fusible, and soluble polymers.

The data for the packing of aromatic polycyanates led to the hypothesis that the mobility of the $C_{sp^3} - C_{sp^2}$ bond between the central carbon atom and the phenyl groups of the internodal fragments of the network exerts the main influence on the physical properties of many of these polymers, differing in the nature of the substituents at the central carbon atom[123].

The packing coefficients have also been calculated[88] for cross-linked polymers based on the dicyanates of oligoarylates, oligosulphones, and oligomeric methylphenyl- and dimethyl-siloxanes with different values of M_C (see Tables 6 and 7). For the majority of polymers investigated as well as for polycyanates based on aryl dicyanates, the packing coefficients are found to be close to k_{av} = 0.681. An exception are polymers containing dimethylsiloxane fragments of different lengths between the network

nodes. These polymers are characterised by anomalously low packing coefficients, decreasing with increase of M_c from 0.651 (for $n = 0$) to 0.587 (for $n = 100$). The fact that the porosity of these systems is zero[88] makes it possible to attribute these anomalously low values to the loose packing of the macromolecules of the organosilicon polycyanates.

The principal parameters of the network structure of polycyanates have been investigated using as an example the polycyanates based on the oligomeric dicyanates (II) and (V) by the method derived from the statistical theory of viscoelasticity[88]. The investigation was performed by measuring the stress relaxation for a constant deformation and biaxial extension of film polycyanate specimens with oligosiloxane ($n = 5$, 25, 50, 70) and oligoarylate ($n = 1$ or 3) internodal fragments. The experimental and calculated parameters of the structures of these polymers are listed in Table 15. Evidently the experimental values of the average (numerical) molecular weight (M_{ce}) and the concentrations of the active chains $(V_c/V)_e$ per unit volume of the cross-linked polymers are close to the theoretical values M_{ct} and $(V_c/V)_t$, which demonstrates the regularity of the networks of the polymers.

Table 15. Parameters of the network structures of polymers based on the oligomeric dicyanates (V) and (II).

n	M_{ce}, g mole^{-1}	M_{ct}, g mole^{-1}	$10^4(V_c/V)_e$, mole cm^{-3}	$10^4(V_c/V)_t$, mole cm^{-3}	$\frac{(V_c/V)_e}{(V_c/V)_t}$
	Polymers based on oligodicyanates (V)				
5	500	800	21.00	13.86	1.50
25	3300	2280	3.00	4.39	0.70
50	4400	4133	2.24	2.36	0.98
70	7300	5614	1.30	1.23	0.74
	Polymers based on oligodicyanates (II)				
1	700	686	16.34	17.35	0.94
3	1100	1352	11.09	8.87	1.25

A very interesting feature of many polycyanates is their capacity for crystallisation. Crystalline cross-linked polymers are known, but their internodal segments were flexible aliphatic and siloxane fragments with M_c of at least 2100 and the crystalline structures of the cross-linked polymers were fully analogous to those of the initial crystalline oligomers and were in essence determined by them[134-139].

Korshak, Pankratov, and coworkers[140] were the first to obtain, using polycyanates, cross-linked, rigid-chain, fine-mesh network polymers with a completely different crystalline structure than that of the initial crystalline monomer: the formation of the crystalline structure of the network polymer takes place during its synthesis. In an X-ray diffraction study of the polycyanate based on 1,4-dicyanatobenzene, the authors[140] showed that, by altering the conditions of synthesis, it is possible to obtain polymers having the same chemical constitution but a different structure. Thus, whereas the specimen obtained in a solvent had a fully amorphous structure, the diffractometer trace for the specimen synthesised in bulk showed additional distinct reflections indicating the formation of a crystalline structure; $M_c = 108$ for this polymer. The authors suggested that, during polycyclotrimerisation in bulk, the polycyanate macromolecules are stacked in the form of parallel corrugated layers. However the tendency towards crystallisation[53-55,123] has also been observed for polycyanates based on a number of other dicyanates (Table 12)†. It appears that, when the initial monomer and the polycyclisation conditions are suitably chosen, structures of this kind can be obtained in a highly crystalline state.

The capacity of polycyanates for crystallisation as well as many other unusual properties of these polymers are a consequence of the regularity of their structure, produced as a result of the highly selective cyclotrimerisation of the N≡C–O groups of the initial monomers and the virtually quantitative completion of the polycyclotrimerisation reaction.

In conclusion, we may note the following fundamental advantages of both polycyclotrimerisation, as a new method for the synthesis of polymers, and of the polycyanates obtained by this method from aromatic and organoelement cyanate esters.

The initial monomers (cyanates) are obtained by a technologically simple procedure from a raw material which is produced industrially. In most cases, these monomers are relatively infusible substances, stable on storage even when catalysts are deposited on them.

Cyanates are polycyclotrimerised both in the presence and absence of catalysts and the process can be interrupted at the stage of oligomers having a consistency ranging from a viscous liquid to solid products readily soluble in many organic solvents (acetone, toluene, alcohol, chloroform, etc.). The manufacture of articles from cyanates in the form of monomers or oligomers is carried out by the traditional methods for the working of thermoreactive polymers without the evolution of volatile materials.

The high selectivity of the reaction and the occurrence of the latter with virtually quantitative conversion of the functional groups are characteristic of the polycyclotrimerisation of cyanates, which makes it possible to obtain regularly cross-linked polymers with strictly specified internodal distances made up of *s*-triazine rings. Polycyanates are therefore the first examples of a series of polymers obtained by polycyclotrimerisation for which it is possible to achieve in practice the hypothetical possibilities of this promising synthesis of polymers, particularly for the preparation of heat-resistant and thermostable materials.

It has been shown for aromatic polycyanates that, in contrast to the randomly cross-linked systems, these polymers possess, by virtue of the regularity of their chemical structure, anomalously high physicomechanical parameters for fine-mesh network rigid-chain polymers of this kind and in many cases are capable of crystallisation.

All these useful qualities of polycyanates as well as their effective adhesion to various materials permit their employment in many fields in modern engineering. Polycyanates are used as plastics[52-55,64,73-77,80,88,97,98,105,145], adhesives[73-77,80,84,85,88,96-99,105,146,147], and binders for glass-fibre-reinforced plastics[55,73-77,80,96,148-151], solid rocket fuel[152], and other materials[153,154] possessing in most cases enhanced heat resistance and thermal stability.

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†It is noteworthy here that this interesting phenomenon has also been observed for rigid highly cross-linked polymers obtained by the polycyclotrimerisation of arylbis(cyanamides)[141-144].

During the preparation of the manuscript for the press, a number of studies devoted to the synthesis [155-158] and properties of polycyanates [159] and the investigation of the kinetics and heats of the polycyclotrimerisation of aryl cyanates were published [160].

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