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Polycarbodiimides

V A Pankratov

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Abstract. The literature data on the synthesis, structure, and properties of a promising class of polyfunctional polymers — polycarbodiimides — are surveyed. The polymerisation reactions of the carbodiimide groups of the polymers and the reactions involving polyaddition to various functional groups with formation of linear and network polymers are described. Certain aspects of the practical use of polycarbodiimides are considered. The bibliography includes 320 references.

I. Introduction

The most promising aspect of the synthesis of heat resistant and thermostable composite polymeric materials is believed at the present time to be their formation from thermoreactive polymers and oligomers capable of being converted into network structures without evolving volatile products.[1–17] Polycarbodiimides, polymers containing the N=C=N groups in the macrochain, are of undoubted interest in this connection.

Carbodiimides can be regarded as alkyl(aryl) derivatives of their simplest representative HN=C=NH, which exists mainly in the tautomeric form $NH_2-C\equiv N$. These compounds belong to the group of heterocumulenes, which comprise a large class of unsaturated compounds based on the allene structure.

Whereas 20 years ago carbodiimides were used solely for preparative purposes, nowadays they are widely employed in various branches of industry, particularly in polymer chemistry. This has been promoted by the discovery of selective catalysts for the decarboxylation of isocyanates, which make it possible to synthesise under mild conditions carbodiimides in virtually quantitative yields.

The preparation of low-molecular-mass carbodiimides and their physical and chemical properties have been described in a series of review articles.[1,18–25] However, to date there have been no surveys of polycarbodiimides and their properties. This review deals with the methods of synthesis of both low-molecular-mass and high-molecular-mass carbodiimides, attention being concentrated on the most promising and technological methods of synthesis, referring precisely to polycarbodiimides, which have been developed in recent years. The structures and properties of polycarbodiimides and of the products of their structure formation reactions are also dealt with in the review as regards the understanding of the principal aspects of their practical applications.

V A Pankratov Laboratory of Thermoreactive Polymers,
A N Nesmeyanov Institute of Organoelement Compounds,
Russian Academy of Sciences, ul. Vavilova 28, 117813 Moscow,
Fax (7-095) 135 50 85

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II. Synthesis of organic and organoelement polycarbodiimides

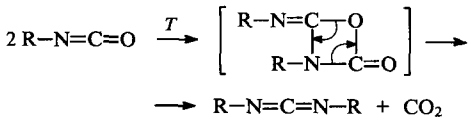
A large number of different methods of synthesis of carbodiimides have now been described in the literature. The principal of these are the desulfurisation of thioureas, the dehydration of urea, and the decarboxylation of isocyanates.[1,18–25]

The commonest method involves the decarboxylation of isocyanates.

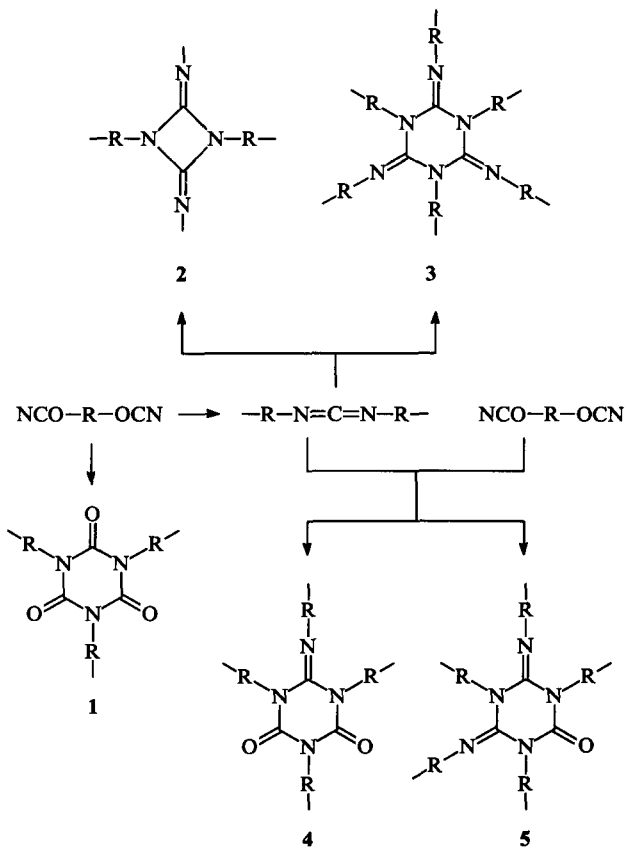
$$2\,R-N=C=O \longrightarrow R-N=C=N-R + CO_2 .$$

At elevated temperatures, this reaction can proceed vigorously even in the absence of catalysts.[26] Certain aromatic carbodiimides, for example, diphenylcarbodiimide (heating of phenyl isocyanate for 24 h at 180 °C), were in fact obtained for the first time in this way.[26] After prolonged heating, diisocyanates afford polycarbodiimides.

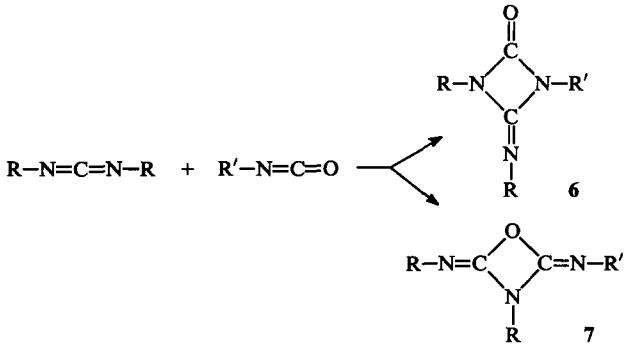
Neuman and Fischer[27] established that the thermal conversion of isocyanates into carbodiimides is autocatalytic and suggested that it proceeds via the formation of intermediate unsymmetric cyclic dimers.



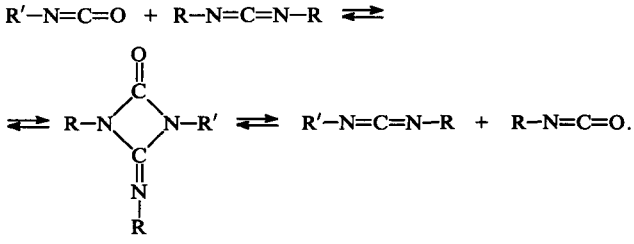
Unfortunately, the purely thermal decarboxylation of isocyanates is accompanied by numerous side reactions, for example the cyclotrimerisation of isocyanates (adduct **1**), the cyclodimerisation and cyclotrimerisation of carbodiimides (adducts **2** and **3**), and the interaction of isocyanates with carbodiimides (adducts **4** and **5**).



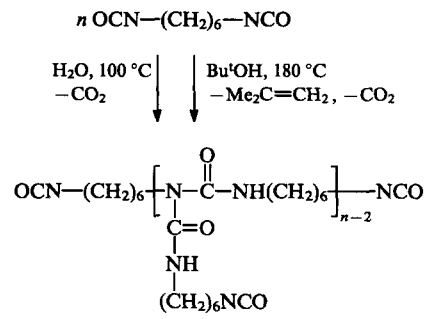
In the study of the reaction of carbodiimides with isocyanates in the absence of oxygen and moisture at 100–160 °C, Neuman and Fischer[27] isolated the unstable cyclic adducts **6** and **7**.



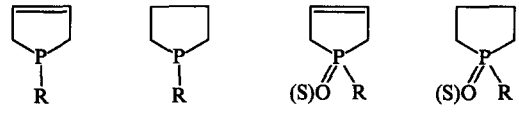
It was shown in the same study that adducts of type **6** (uretone imines) decompose on heating to an isocyanate and a carbodiimide with exchange of substituents in accordance with the following scheme:



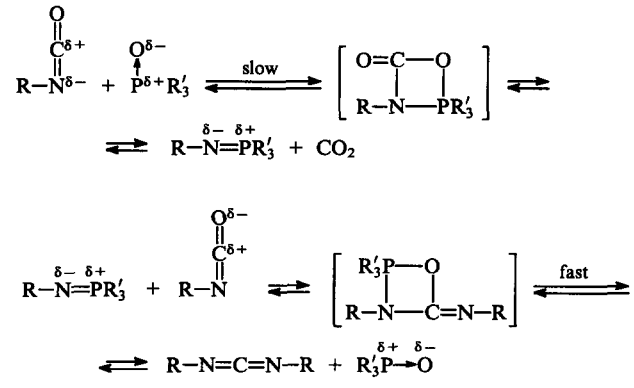
Acceleration of the decarboxylation reaction can be achieved by adding small amounts of water, *tert*-butyl alcohol, and mono- and di-amines to the reaction mixture. Polyisocyanates **8**, with a biuret main chain, have been obtained.[28] They function as catalysts of the carbodiimide formation reaction.



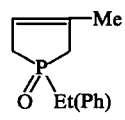
Numerous compounds have been proposed as catalysts, but the highest catalytic activity was found for P-substituted phosphacyclopentenes (phospholenes) **9** and phosphacyclopentanes (phospholans) **10**[29] as well as the *P*-oxides or sulfides **11** and **12**.[30–32]



The mechanism of the catalytic conversion into a carbodiimide has been investigated[33–36] and a two-stage mechanism has been proposed for the process.



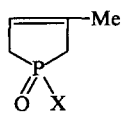
By comparing the catalytic activities of various phosphorus compounds in the carbodiimide formation reactions, Monagle et al.[36] established the following activity series: phosphine oxides > phosphinates > phosphonates > phosphates. Tertiary phosphine oxides, containing the phospholene ring, proved to be the most active.[29,34–38] The use of these catalysts ensured the formation of pure carbodiimides under mild conditions (60–100 °C) in high yields. 1-Ethyl-1-oxo- and 1-oxo-1-phenyl-3-methylphospholenes have been used most frequently as catalysts.



The ethyl derivative proved to be the most active but the phenyl derivative is most readily available.

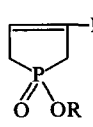
Much work has been done by Arbuzov and co-workers in the study of the influence of the structures of various phospholene derivatives on the catalytic activity in the carbodiimide formation reaction.[39] The catalytic activity in the series of phospholene-phosphinic acids was estimated from the rate constants for the conversion of phenyl isocyanate into diphenylcarbodiimide in solution in toluene at 20 °C.

It was shown that the conversion of the esters **14** (X = OR) into the amides (X = NR_2), the replacement of the alkyl group R in the esters by an aryl or alkylaryl group, the migration of the double bond in the ring, as well as the presence or absence of substituents at the carbon atoms of the phospholene ring induce only slight changes in the reaction rate constant [$k = (0.8-3.0) \times 10^4\ s^{-1}$]. On the other hand, all the compounds investigated are significantly inferior as regards catalytic activity to phospholene oxide (X = Ph) ($k = 68.6 \times 10^4\ s^{-1}$). On the basis of the results obtained, the authors[39] propose the following catalytic activity series: phospholene oxides > phospholenephosphinates > acyclic phosphine oxides > phosphinates.

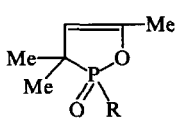


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Subsequently Arbuzov and coworkers[40] investigated the influence of the environment of the phosphorus atom in organophosphorus compounds on their catalytic activity in carbodiimide formation reactions. The conversion of phenyl isocyanate into diphenylcarbodiimide at 242 °C in the presence of derivatives of phospholene **15** and oxaphospholene **16**, containing the same numbers of P–C and P–O bonds, was chosen as the model reaction.



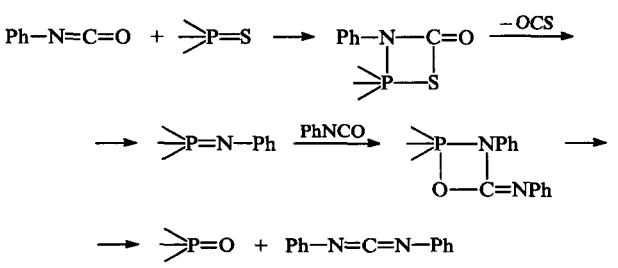
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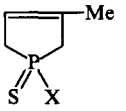
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The replacement of the phospholene isomer by the oxaphospholene isomer led to a significant decrease in the catalytic reaction rate constant (from 17×10^4 to $3.8 \times 10^4\ s^{-1}$ for R = Et and from 14×10^4 to $0.8 \times 10^4\ s^{-1}$ for R = Ph). The conversion of exocyclic esters into amides (–NR_2 instead of –OR) caused by a further decrease in the carbodiimide formation reaction rate constant—approximately by a factor of two. The specific properties of phospholene derivatives, ensuring the maximum catalytic activity, were thereby confirmed.

The replacement of the oxygen atom by a sulfur atom in phospholene oxides also diminished greatly the catalytic activity of these compounds. Kinetic experiments carried out on phosphoryl and thiophosphoryl compounds revealed a significant difference in the mechanisms of the reactions involving these compounds.[40] In the case of thiophosphoryl compounds, the plot of the relation $\ln(1-P)^{-1} = f(\tau)$ (P is the degree of conversion and τ the time) showed an inflection, which indicated an increase in the activity of the catalyst during the process. The following reaction mechanism was proposed:



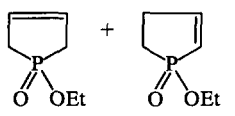
The phosphoryl catalyst accumulated during the reaction, increasing the overall reaction rate constant. The authors therefore determined two reaction rate constants: k_1 at the beginning (when the content of the phosphoryl compound was low) and k_2 at the end of the reaction (when virtually the entire thiophosphoryl catalyst was converted into the phosphoryl catalyst). For initial catalysts of the type



the ratio of the rate constants for the condensation of phenyl isocyanate at 442 K changed from ~1.5 (X = OEt) to ~6.5 (X = SEt). Guberman et al.[41] investigated the influence of the structure of the phospholene catalysts **13**, **17**, and **18** and of substituted initial phenyl isocyanates $X-C_6H_4-N=C=O$ on the kinetics of the conversion of the latter into carbodiimides.



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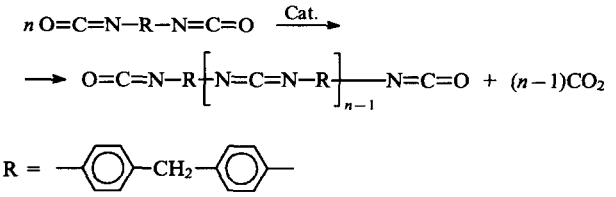
The reactions were carried out in benzene or toluene at concentrations of the isocyanates and the catalysts of 1 kmol m^{-3} and 0.04 kmol m^{-3} respectively. The catalyst **13** proved to be significantly more active than the catalysts **14** and **15**, which agrees well with the results of previous studies. The influence of the substituents (X) on the reactivities of substituted phenyl isocyanates was determined from the results.

$$o\text{-Cl} < H < p\text{-Cl} < m\text{-Cl} < m\text{-}CF_3 < m\text{-}NO_2 .$$

The relation obtained agrees well with the reaction mechanism proposed previously[33–36] (electron-accepting substituents, with the exception of those giving rise to steric hindrance, facilitate the nucleophilic attack of the phosphoryl group on the carbonyl carbon atom of the isocyanate).

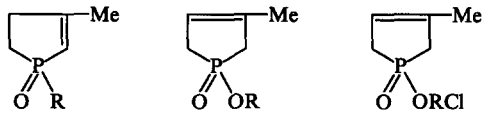
Aliphatic carbodiimides have also been obtained[33] in reactions catalysed by oxaphospholenes but at higher temperatures and in lower yields. Thus n-butyl isocyanate was converted into di-n-butylcarbodiimide to the extent of only 17% on refluxing for 20 h with 1.4 mol.% of 1-ethyl-3-methyl-1-oxo-3-phospholene. The yield was increased to 60% by carrying out the reaction in high-boiling solvents. The reaction was faster for high-boiling aliphatic isocyanates. For example, 2-octyl isocyanate was converted after 2 h at 413–433 K into the corresponding carbodiimides to the extent of 89%.

The influence of the chemical structures of a series of phospholene oxides on the rate of formation of polycarbodiimide



from bis(4-isocyanatophenyl)methane has been estimated.[42]

Derivatives of 3-methyl-1-oxophospholene of three types were used as catalysts: tertiary phosphine oxides **19**, phosphinates with unsubstituted ester groups **20**, and phosphinates with haloester groups **21**.

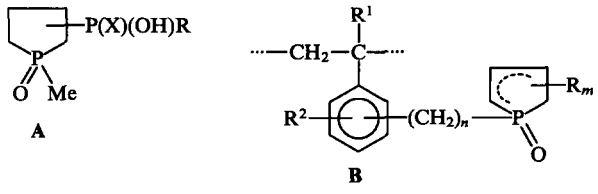


19 20 21

In all cases, the reaction was carried out in benzene at 353 K and diisocyanate and catalyst concentrations of 1 and 0.02 kmol m^{-3} respectively.

It was found that the catalytic activities of the phospholene derivatives investigated depend significantly on the catalyst structure, primarily on the nature of the exocyclic substituent at the phosphorus atom. Compounds **19** exhibited the highest catalytic activity. When the phosphinates **20** were used, the reaction rate constant fell by a factor of approximately 50. The haloesters **21** were found to be even less active. Thus the dependence of the rate constants for the carbodiimide formation reaction on the electronegativity of the substituents at the phosphorus atoms was also observed for the series of compounds investigated, as had been found for monoisocyanates.[39-41]

Insoluble polymeric catalysts for the condensation of isocyanates have found extensive application. They were synthesised in two ways. The first is based on the addition of soluble derivatives of phospholene oxides **A** (R = OH, Me; X = O, S) to an ion-exchange matrix with formation of insoluble high-molecular-mass carbodiimide formation catalysts.[43-46] The second procedure is based on the chloromethylation of the styrene–divinylbenzene copolymer (molar ratio 98:2).[47] The product thus obtained was treated, for example, with 1-chloro-3-methyl-3-phospholene, catalysts containing the repeating unit **B** (where R = Hal, Alk, AlkO, PhO, HalAlk; R^1 = H, Me; R^2 = radical not containing substituents interacting with isocyanate groups; m = 1–3; n = 0, 1) being obtained after oxidation with hydrogen peroxide.



A B

Since the polymeric catalysts are less active than the soluble phospholene derivatives, the condensation of isocyanates in their presence was carried out at higher temperatures (413–423 K). The advantages of the polymeric catalysts include the possibility of repeated use and the possibility of obtaining stable polycarbodiimides not containing an admixture of the catalyst.[43-50]

Apart from the phospholene derivatives, it has been suggested that acyclic trialkyl phosphine oxides,[51-53] phosphates,[51-54] alkoxyphosphines,[55] and triphenyl-n-butylphosphonitrobromide [bromo(n-butyl)triphenylphosphorane (Translator)],[56] as well as the product of the interaction of a bicyclic terpene (camphene) with dichlorophenylphosphine[57] be used as carbodiimide formation catalysts.

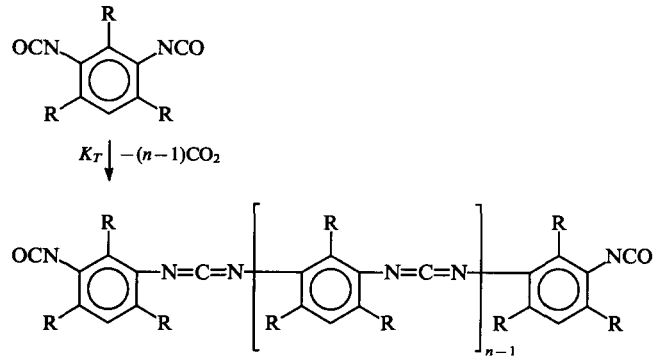
Certain organic compounds of arsenic, containing the highly polarised As–O bond, for example triphenylarsine oxides, also exhibit a fairly high catalytic activity.[51]

In order to obtain insoluble arsenic-containing catalysts, brominated or chlorinated polystyrene was treated with diphenylarsonium chloride and then oxidised with hydrogen peroxide. The polymers obtained contained the $AsO(C_6H_5)_2$ and $CH_2AsO(C_6H_5)_2$ groups. These catalysts were used to obtain low-molecular-mass carbodiimides from bis(4-isocyanatophenyl)-methane.[58-60]

It has been suggested that derivatives of *s*-triazine[61-65] or their mixtures with derivatives of hexahydro-*s*-triazine[66] as well as dialkyl sulfates, sulfites, or sulfoxides[67] be used as catalysts for the condensation of diisocyanates in industry, especially in the manufacture of polyurethane foams containing a controllable amount of carbodiimide groups.

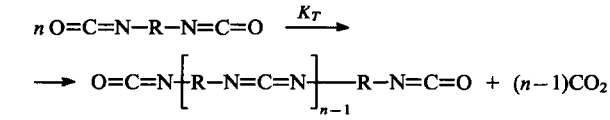
Despite the fact that the chemistry of carbodiimides has developed over a period of over 100 years, these compounds have found practical applications only recently. There is no doubt that this is to a large extent associated with the discovery of the possibility of obtaining polymeric carbodiimides from the corresponding industrial diisocyanates. The interest shown in polycarbodiimides is due to their high thermal stability and heat resistance and satisfactory physicomechanical parameters.

Neuman and Fischer[27] obtained by the catalytic condensation of isocyanates in the presence of phospholene oxides oligomeric ($M \leqslant 2000$) α,ω-diisocyanatopolycarbodiimides with aliphatic substituents in aromatic nuclei, which prevented the formation of cross-linked structures.



R = Me, Et, Pr^i.

Campbell and Smeltz[68] synthesised polycarbodiimides by the polycondensation of aromatic diisocyanates in hydrocarbon solvents in the presence of 1-ethyl-3-methyl-1-oxo-3-phospholene.[68]



R = Ar.

Polycarbodiimides have been synthesised by the polycondensation of a series of aromatic and aliphatic diisocyanates in hydrocarbon solvents or in mixtures with dimethyl sulfoxide (metastable solutions were formed in the latter case) in the presence of 3-methyl-1-oxo-1-phenyl-3-phospholene.[69] The polymers had high softening temperatures (200–350 °C) and were converted into pale-yellow films by pressing under pressure. Aliphatic polycarbodiimides formed weak and brittle films, whereas films based on aromatic polycarbodiimides were strong and rigid.

In order to reduce the softening temperatures of the polycarbodiimides and to obtain soluble polymers, it has been suggested that the polycondensation of diisocyanates be terminated at the stage involving the formation of low-molecular-mass oligomers. The reaction was carried out after a definite degree of conversion (3%–60%) of isocyanate groups into carbodiimide groups with subsequent cooling of the reaction mixture.[46,53,59,60,70-74] Liquid diisocyanatooligocarbodiimides based on bis(4-isocyanatophenyl)methane were synthesised in this way. They are stable during storage for 3–6 months.[60,70,75-78]

Studies on the synthesis of carbodiimide-containing polymers with a specified molecular mass by the introduction of monofunctional isocyanates into the reaction system are of considerable interest.[1,78-82] It was shown that the thermal characteristics of the polymers, synthesised from a mixture of di- and

mono-functional isocyanates, are close to the characteristics of high-molecular-mass carbodiimides based on diisocyanates alone. The polymers obtained for the molar ratios of the di- and mono-functional isocyanates ranging from 6:1 to 20:1 have a mechanical strength close to that of the high-molecular-mass polymer. The softening temperatures of such polymers were in the range 230–260 °C and the decrease in mass on heating in air at 300 °C was ~2% (at a heating rate of 15 K min $^{-1}$).[79]

Polycarbodiimides with an exceptionally high thermal stability have been obtained by the joint condensation of various aromatic diisocyanates.[24] For example, the copolymers of *p*-phenylene diisocyanate and 1,5-naphthylene diisocyanate had a softening temperature of about 300 °C. The average molecular masses of these α,ω-diisocyanatopolycarbodiimides were low, since limiting solubilities in inert solvents are reached with increase in the molecular mass of the polymers and the latter precipitate from the solution. After this, the increase in molecular mass ceases. Ternary mixed polycarbodiimides, consisting of 2,4-tolylene diisocyanate and the aromatic diisocyanates indicated above in proportions of 1:1:1, had average molecular masses of about 3500.

It has been established[24] that oligomeric α,ω-diisocyanatocarbodiimides are formed from 2,4-tolylene diisocyanate at room temperature in the presence of phospholene oxides as catalysts. Wagner et al.[24] synthesised a homologous series of carbodiimide oligomers based on 2,4-tolylene diisocyanate by fractionation in cyclohexanone or in a petroleum ether–hexane mixture. The oligocarbodiimides obtained in this way are of interest for use in polymer-analogue reactions.

The synthesis of organoelement polycarbodiimides $[-E-N=C=N-]_n$, the N=C=N groups of which are linked directly to the atom of the [inorganic] element, differs fundamentally from the synthesis of organic polycarbodiimides.

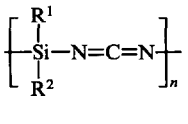
Thus polymeric silicon-containing carbodiimides are formed from silver cyanamide and dialkyl- or diaryl-dichlorosilanes.[83] The tetramer of dibutylbis(carbodiimido)stannane has been obtained similarly from $Bu^n_2SnCl_2$.[84]

$$n\,Ag_2NC{\equiv}N + n\,RR'MCl_2 \longrightarrow \longrightarrow \left[MRR'-N=C=N\right]_n + 2n\,AgCl$$

M = Si; R = Me, Ph, EtO; R′ = Me, Ph, Vinyl, EtO;
M = Sn; R = R′ = Bu; *n* = 4.

The corresponding polysilylcarbodiimides have been synthesised from dicyanodiamide and polysilazanes.[85]

Oligomeric silicon carbodiimides have been obtained by heating $Me_3SiN=C=NSiMe_3$ with dihalosilanes, trihalosilanes, or haloorganosiloxanes with simultaneous distillation of the Me_3SiCl evolved.[86,87]



R^1 = Me, Ph; R^2 = Ph.

A distinctive feature of polysilylcarbodiimides is the direct linkage between the carbodiimide group and the silicon atom, which alters significantly the reactivity of the former. In contrast to organic analogues, such compounds can react not only via the carbodiimide group but also via the silicon–nitrogen bond.

The oligomers obtained are highly viscous liquids or solids at room temperature. Their molecular mass, determined by the ebullioscopic method, is in the range 3000–5000, which corresponds to a polarisation coefficient in the range 15–25. Polysilylcarbodiimides exhibit a high thermal stability and do not undergo structure formation on heat treatment in contrast to their aromatic analogues. They do not lose mass on heating to 400 °C and retain their solubility in organic solvents under these conditions. The IR spectra of the initial polydiphenylsilylcarbodiimides and those heated at 350 °C for 2 h hardly differ. The temperature of the onset of the decrease in mass is 450 °C for these polymers. Oligomeric polysilylcarbodiimides contain a fairly high percentage of coke (up to 30% at 900 °C).[86,87]

In order to investigate the influence of the relative content of rigid aromatic and flexible siloxane units on the properties of oligocarbodiimides, the copolymers of aromatic diisocyanates—4,4′-bis(isocyanatophenyl)methane and 2,4-tolylene diisocyanate—with organosilicon macrodiisocyanates were obtained.[88] The molar ratio of the aromatic and organosilicon macrodiisocyanates varied from 0–1 to 50–1 (moles). Thermal and physicomechanical studies on these polymers showed that their properties depend significantly on the ratio of the starting materials taken for the reaction (Table 1).

Table 1. The properties of the linear copolymers obtained by the polycondensation of di(4-isocyanatophenyl)methane (**A**) and an organosilicon macrodiisocyanate (n = 14) (**B**) for different proportions of the starting materials.[88]

Molar ratio **A**:**B**	η_{int}/dl g^{-1}	Yield (%)	T_{soft}/°C	σ_t/kgf cm^{-2}	ε (%)
0:1	0.63	92	−84	72	118
10:1	–	93	140	190	95
20:1	0.84	89	160	240	70
30:1	–	95	170	300	45
40:1	0.89	96	180	350	20
50:1	–	94	190	420	10
C[a]	0.9	–	280	500	5

[a] The thermal and physico-mechanical parameters of the linear aromatic polycarbodiimide based on di(4-isocyanatophenyl)methane (**C**) are included for comparison.

The data presented show that the carbodiimides can be obtained by easy and varied procedures, in many instances in high yields. The practical value of polycarbodiimides consists in their high reactivity in relation to many organic compounds, which makes it possible to obtain from them a wide variety of polymeric materials, including those with high thermal stabilities and heat resistances. Therefore we shall consider below their structural features and also their physical and chemical properties.

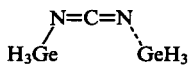
III. The structure and certain physical properties of polycarbodiimides

According to X-ray diffraction data, the carbodiimide group is not linear, the N=C=N angle varying in the range from 166° to 170° for both aliphatic and aromatic carbodiimides.[89–93] The dihedral angle between the substituents at the nitrogen atom is approximately 90°, but the C=N–Ar angle exceeds the expected value of 120° and varies in the range 123°–180°.

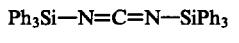
The anomalous value of the N=C=N angle has been explained[89] by the influence of the packing factors in the crystals. However, the fact that all the carbodiimides investigated[89–93] exhibit such anomaly casts doubt on the validity of this explanation. It has been shown that in other heterocumulenes the X=Y=Z triatomic group has a not entirely linear structure. Thus a microwave spectroscopic study of chlorine azide (ClN_3) yielded a N=N=N angle of ~172°.[94] According to microwave spectroscopic data and quantum-chemical calculations, the isocyanate group is also non-linear, the O=C=N angle amounting to 171°–175° depending on the nature of the group at the nitrogen atom.[95–97]

These data indicate that the bent structure of the carbodiimide group can arise also as a result of electronic effects and not only due to crystal packing effects.[22]

The results of both electron diffraction[98] and X-ray diffraction[99] studies on organoelement carbodiimides indicate the existence of nonlinear and linear structures of digermylcarbodiimide **22** and bis(triphenylsilyl)carbodiimide **23** respectively.



22



23

An electron diffraction study has also indicated a linear configuration of the NCNSi group in disilylcarbodiimide.[100]

The electronic structures and stereochemistry of aliphatic and organoelement low-molecular mass carbodiimides as well as nuclear magnetic resonance, IR, photoelectron, and UV spectroscopic, and mass-spectrometric data for these compounds have been examined in detail in a series of reviews,[18-25] so we need not dwell on their discussions in the present review. However, the physicochemical characteristics of high-molecular-mass carbodiimides merit a more detailed description.

Linear high-molecular-mass carbodiimides, obtained under mild conditions, exhibit film- and fibre-forming capacities, possess high thermal characteristics and effective strength parameters, and are resistant to the action of corrosive liquids.[68,69]

The effective physico-mechanical and dielectric properties of polycarbodiimides may be illustrated in relation to the film of poly(3,3'-dimethoxy-4,4'-diphenyl)carbodiimide obtained by pressing at 300 °C and oriented at 115 °C.

Initial modulus of elasticity/kgf cm^{-2} †	86200
Tensile strength/kgf cm^{-2}	2900
Elongation (%)	6.2
ε ($10^2 - 10^5$ Hz)	3.8 (170 °C)
tan δ ($10^2 - 10^5$ Hz)	0.006–0.02 (170 °C)

The study of the thermal properties of polycarbodiimides with blocked terminal groups established that oligocarbodiimides are characterised by a satisfactory fluidity in the temperature range 240 –270 °C, their fusion being accompanied by an increase in the viscosity of the melt and the transition of the specimen to the highly elastic state.[80] An increase in the viscosity of the melt with increase in the molecular mass of the initial oligocarbodiimide has been noted. Polycarbodiimides based on di(4-isocyanatophenyl)-methane have a glass point of 220 °C and pass to the highly elastic state at 250 °C, a further increase in temperature leading to an increase in the modulus of elasticity.

The preparation of polycarbodiimides and layered plastics based on them, containing reinforcing fibrous fillers, has been discussed.[101] The polycarbodiimides were obtained by heating di(4-isocyanatophenyl)methane at 20–150 °C in solution, for example in benzene, in the presence of 3-methyl-1-phenyl-2-phospholene 1-oxide with subsequent addition of monoisocyanates. The decrease in the mass of the resulting polymers in air (thermogravimetric analysis, heating rate 10 K min^{-1}) at 250 °C and 300 °C was 0.7% and 1.7% respectively. The polymer specimens, obtained by pressing in preheated moulds at 180–200 °C, had a tensile strength of 680 kgf cm^{-2}, a modulus of elasticity on extension of 10 100 kgf cm^{-2}, an elongation of 7%, and a glass point of 208 °C.

Polymeric organosilicon carbodiimides of the type $[-SiRR'N=C=N-]_n$, where R,R' = Me, Ph, or vinyl, obtained by the reaction of polychlorosilanes, or chlorosilanes with $Me_3SiN=C=NSiMe_3$, are colourless or pale-brown products, which on heating above 100 °C are gradually converted into viscous oils. Their thermal stability is apparently determined by the presence of a certain number of siloxane units in the macromolecular chain,[83] because the onset of the loss of mass by these products is observed already at 200 °C. The IR spectra of the specimens hardly change even on heating up to 350 °C for 2 h *in vacuo*, which indicates a higher thermal stability of the silylcarbodiimide groups.

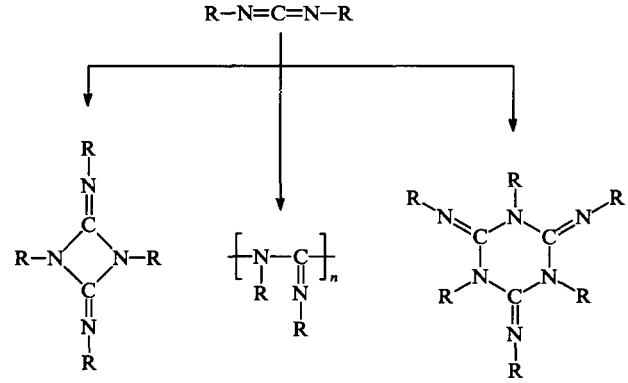
Organoelement carbodiimides possess N=C=N groups which are much more stable as regards polymerisation than in their organic analogues; silicon-, germanium-, tin-, and lead-containing monocarbodiimides can be stored virtually without change for many months.[102] Under these conditions, an increase in viscosity as a consequence of polymerisation, which is so characteristic of organic carbodiimides, is not observed. Organosilicon monocarbodiimides can be as a rule vacuum-distilled without decomposition at 250–260 °C.[102] This can be explained by the increased strength of their Si–N bond as a result of the $d_\pi - p_\pi$ interaction of the silicon and nitrogen atoms.[103]

Organosilicon polycarbodiimides are stable when irradiated, which makes it possible to use them under the conditions of intense irradiation. For example, mass loss is not observed for the polysilylcarbodiimide $[-Ph_2SiN=C=N-]_n$ with a molecular weight of 4285 on heating to 400 °C under a nitrogen atmosphere and it retains its elasticity on irradiation with a dose of 2000 Mrad.[86]

IV. Chemical properties of polycarbodiimides

The chemical properties of carbodiimides are determined primarily by the highly unsaturated nature of these compounds and hence by their tendency to undergo polymerisation and addition reactions.

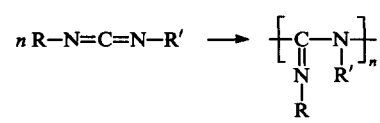
Like isocyanates, carbodiimides are capable of polymerising via the nitrogen–carbon bond with formation of linear polymers, and also of cyclodimerisation and cyclotrimerisation.[1,18-25]



Unfortunately, these interesting reactions have been inadequately investigated and there exist only a limited number of communications on this topic in the literature.[79-82,104-110]

1. Linear polymerisation of carbodiimides

The anionic polymerisation of carbodiimides, analogous to the polymerisation of isocyanates,[111] was first reported by Robinson.[112]



R, R' = Et, Bu, Hex, All, Ph.

† 1 kgf cm^{-2} = 0.9807 × 10^5 Pa.

The reaction was carried out in hydrocarbon solvents in the presence of n-butyllithium at 0–25 °C. Table 2 presents certain data on the polymerisation of carbodiimides and on the properties of the resulting polymers.

Table 2. The properties of the polymers obtained by the anionic polymerisation of carbodiimides.[112]

R	Solvent	Molar ratio monomer: catalyst	η_{int}[a]/dl g^{-1}	Yield of polymer (%)
Et	toluene	270	0.41	37[b]
	"	33	0.20	62
	[c]	–	0.22	–
Ph	toluene	17	0.11	60
$CH_2-CH=CH_2$	"	37	0.13	92
Bu^n	n-heptane	15	0.15	96
n-C_6H_{13}	"	15	0.12	90
Me	"	38	0.14	95

[a] Intrinsic viscosity in formic acid at 30 °C.
[b] Onset of polymerisation at 25 °C and then at 0 °C.
[c] Thermal polymerisation in the absence of a solvent.

The polymers are white powders insoluble in organic solvents. On heating, they partly decomposed to the initial monomers, the greatest thermal stability being shown by the polymers based on diphenylcarbodiimide. It has also been observed[112] that cationic catalysts do not polymerise carbodiimides but form ionic compounds with the latter.

$$p\text{-}BrC_6H_4SO_2Cl + R{-}N{=}C{=}N{-}R' \longrightarrow \longrightarrow \left[p\text{-}BrC_6H_4SO_2{-}\overset{R}{\underset{|}{N}}{-}\overset{+}{C}{=}N{-}R'\right]Cl^-$$

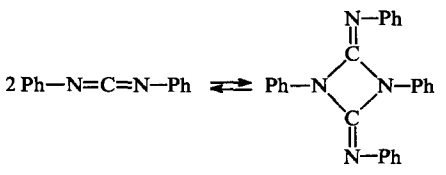
The characteristic features of the linear polymerisation of monocarbodiimides suggest that polycarbodiimides can react similarly, but such data are not available in the literature.

2. Polymerisation of mono- and poly-carbodiimides with formation of cyclic structures

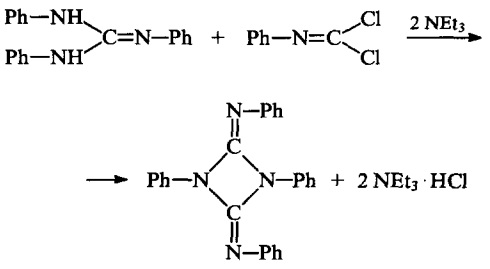
Since the study of the structures of network polymers, formed on polymerisation of polycarbodiimides, presents considerable difficulties, at the beginning of this section we shall consider studies devoted to the cyclodimerisation and cyclotrimerisation reactions of monocarbodiimides as well as studies on the low-molecular-mass structures of the resulting individual products. Investigation of such systems, modelling the corresponding processes in polymers, helps to interpret the more complex structures of the network polymers obtained from polycarbodiimides.

a. Cyclodimerisation and cyclotrimerisation of monocarbodiimides

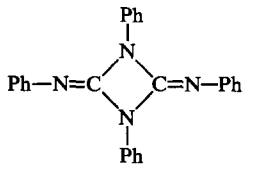
The cyclodimerisation of carbodiimides based on diphenylcarbodiimide has been investigated by Richter.[113] It was found that it occurred on heating even in the absence of a catalyst.



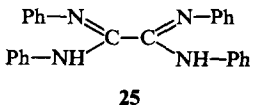
With increase in the reaction temperature, the yield of the dimer also rose, reaching a maximum at 165–175 °C (43% after 16 h). A further increase in temperature reduced the yield to 30% at 200 °C and 13.5% at 230–235 °C. On the basis of these results, Richter suggested that the thermal dimerisation of diphenylcarbodiimide is reversible. Tertiary phosphines proved to be its active catalysts. By adding, for example, tri-n-butylphosphine, it proved possible to attain a yield of the dimer of 75% at a reaction temperature of only 90 °C. In order to demonstrate the cyclic structure of the diphenylcarbodiimide dimer, Richter carried out its unambiguous synthesis[113] by the reaction of triphenylguanidine with phenyl isocyanide dichloride [*N*-phenylcarbonimidic dichloride (Translator)].



Tsuzuki and Iwakura[114] investigated the reactions of diphenylcarbodiimide in the presence of sodium naphthenate in an aprotic solvent, leading to the formation of both cyclic and linear structures. The cyclic dimer **24**, with a characteristic band due to the stretching vibrations of the ring C=N bond at 1690 cm^{-1}, as well as the linear dimer **25**, the structure of which was characterised on the basis of the IR absorption band near 1637 cm^{-1}, were obtained, isolated, and identified.



24

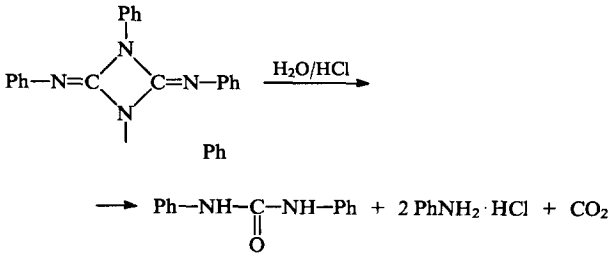


25

The authors[114] showed that the structure of compound **25** is formed in the presence of considerable amounts of sodium naphthenate and of protons in the reaction mixture. The formation of the diphenylcarbodiimide trimer was not observed under the conditions investigated.

There are also other examples of the study of the dimerisation of carbodiimides.[115–117]

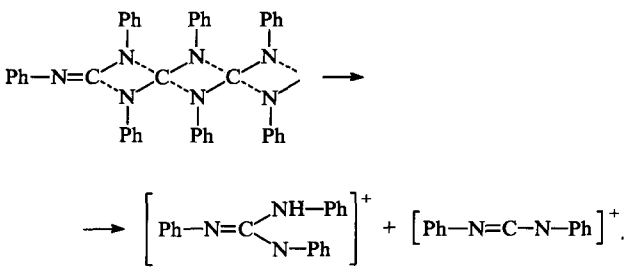
Pankratov et al.[118] synthesised the diphenylcarbodiimide dimer by prolonged heating of diphenylcarbodiimide at 160–170 °C in the absence of a catalyst. The product recrystallised from a 1 : 1 (by volume) benzene–ethanol mixture consisted of a white powder with a melting point of 162.5–163 °C. It was readily soluble in benzene, chloroform, and acetone. The diphenylcarbodiimide dimer was identified[118] by mass spectrometry and IR spectroscopy (the C=N bond absorption band at 1690 ± 10 cm^{-1}) and also on the basis of the composition of the hydrolysis products.



As early as the last century, it was known[119] that diphenylcarbodiimide polymerises slowly at room temperature with formation of the so called 'β-diphenylcarbodiimide', to which a trimeric structure was attributed.[120] The structure of this compound has not been established up to the present time apparently owing to its sparing solubility in organic solvents and instability on heating. Richter[113] obtained 'β-diphenylcarbodiimide' in a high yield by heating diphenylcarbodiimide in the presence of catalytic amounts of tris(diethylaminomethyl)-phosphine.

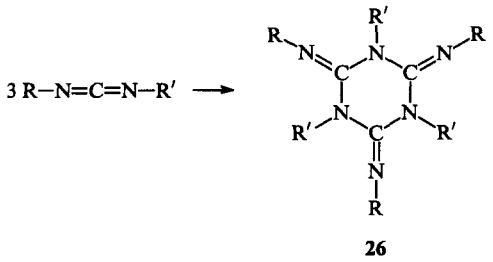
An attempt has been made[118] to identify 'β-diphenylcarbodiimide'. According to the authors,[118] their structure of 'β-diphenylcarbodiimide' agrees with IR spectroscopic data and the results of hydrolysis in the presence of hydrochloric acid and explains the sparing solubility of this compound in organic solvents in the cold as well as its low stability on heating.

The peaks due to ions with m/e = 286 (intensity ~1%) and with m/e = 194 (intensity ~100%) were observed in the mass spectrum of 'β-diphenylcarbodiimide'. Taking into account the structure of this compound proposed in the above study, the mechanism of its decomposition by electron impact has been represented as follows:[118]



However, the above structure of 'β-diphenylcarbodiimide' still remains only tentative.

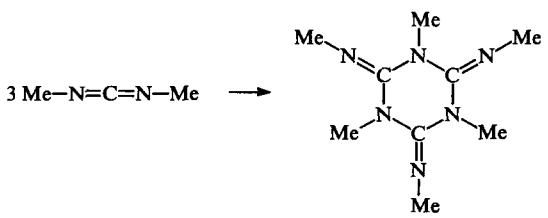
The cyclotrimerisation of carbodiimides with formation of derivatives of 1,3,5-hexahydro-2,4,6-triazine **26** is one of some comparatively little investigated reactions.[104,105,110,117,118,121–124]



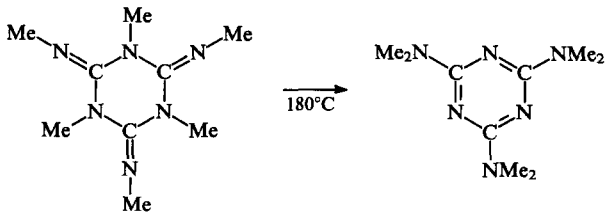
26

According to Busch and coworkers,[121,122] the cyclotrimerisation of diphenylcarbodiimide with formation of a cyclic trimer (hexaphenylisomelamine) takes place when dry hydrogen chloride is passed into a benzene solution of diphenylcarbodiimide containing a small amount of phenol.

The cyclotrimerisation of dimethylcarbodiimide has been reported.[106]

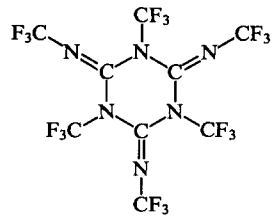


On heating to 180 °C, the isomelamine form **27** of the trimer is converted into the more stable melamine form **28**.



27 **28**

In the course of their synthesis of fluorinated carbodiimides by the reaction of $F_3C-N=CF_2$ with equimolecular amounts of amines RNH_2, Flowers et al.[117] isolated compound **29** as a side product.

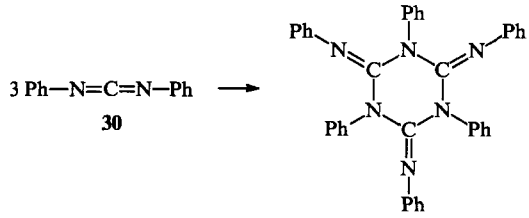


29

Hexaphenylisomelamine has also been isolated after heating phenyl isocyanate with *N*-methylhexamethyldisilazane.[125]

The literature contains a series of communications describing the cyclotrimerisation of carbodiimides with azomethines,[126,127] isocyanates,[128,132] acyl isocyanates,[133] chlorosulfonyl isocyanates,[134] and isothiocyanates,[135] which leads to the formation of *s*-triazine derivatives.

Pankratov et al.[118] obtained hexaphenylisomelamine **31** with a melting point of 196–196.5 °C by the cyclotrimerisation of diphenylcarbodiimide **30**.



30 **31**

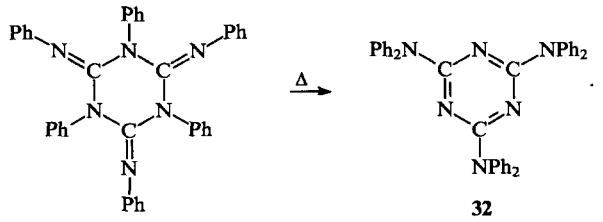
Comparison of the thermal stabilities of derivatives of diphenylcarbodiimide enabled Pankratov et al.[118] to arrange them in a series in terms of increasing thermal stability: 'β-diphenylcarbodiimide' < dimer < hexaphenylisomelamine.

'β-Diphenylcarbodiimide' decomposed on heating above 100 °C in the presence of high-boiling organic solvents, for example 1,1,2,2-tetrachloroethane. Its only decomposition product was diphenylcarbodiimide.[118]

The dimer melted without decomposition at 162.5–163 °C and decomposed vigorously only on heating above 200 °C. Diphenylcarbodiimide was obtained in 80% yield on thermal decomposition of the dimer at 250 °C.

Hexaphenylisomelamine underwent no changes whatever even on prolonged (40 h) boiling in high-boiling liquids, for example in *N*-methyl-2-pyrrolidinone, decalin, and benzyl alcohol. In contrast to triphenylisomelamine,[136] it does not

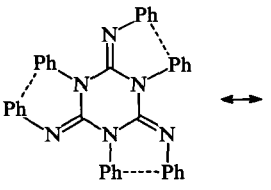
isomerise to the melamine derivative on heating in benzyl alcohol in the presence of alkali metal alkoxides. On heating in the absence of solvents, hexaphenylisomelamine is stable up to 300–320 °C. However, on heating at a higher temperature for 12 h under an inert atmosphere, hexaphenylmelamine was nevertheless obtained in 80% yield.[118]



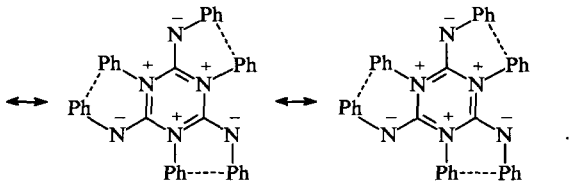
32

In order to elucidate the causes responsible for the thermal isomerisation of the iso-form of hexaphenylmelamine to the normal form and to explain the greater thermal stability of the latter, the structures of the isomeric hexaphenylmelamines were investigated by X-ray diffraction.[104] It was established that the central heterocycle of the iso-form (Fig. 1) is nonplanar and has the configuration of a skewed flattened boat. In contrast to the planar configuration of the heterocycles in analogous compounds (cyanuric acid[139,140] and triphenyl isocyanurate[141]), such nonplanar configuration is probably a consequence of intramolecular steric strain. Distortions of the plane of the exocyclic bond angles and also distortions of the plane of the exocyclic C=N double bonds, the torsional angles of which reach 20°, indicate the phenyl–phenyl steric interactions. Such twisting is usual in the presence of bulky substituents at a double bond.[142] The steric repulsion in pairs of phenyl substituents proved to be so great that the C(21), C(41), and C(61) atoms were displaced from the average plane of the neighbouring atoms to the extent of approximately 0.06 Å, but the configuration of the C(11), C(31), and C(51) atoms remained virtually planar.[104]

The lengths of the endocyclic C–N bonds in the hexaphenylisomelamine molecule (d_{av} = 1.398 Å) are intermediate between the lengths of single (1.47 Å) and double (1.23 Å) carbon–nitrogen bonds. This fact is partly due to the contribution to the molecular structure of hexaphenylisomelamine, apart from that of the main form **33**, also by the resonance forms **34** and **35** with alternation of double and single bonds in the heterocycle (the intramolecular contacts between the phenyl substituents are indicated by dashed lines in the formulae below).



33



34 35

The lengthening of the C–N exocyclic bonds on average to 1.267 Å is also associated with the contribution of the resonance forms **34** and **35**.[104]

In hexaphenylmelamine **31**, the atoms of the heterocycle as well as the exocyclic nitrogen atoms are located in a single plane (Fig. 2). The structure of this compound is of the usual type for n-melamine derivatives. The greater rotation of the benzene rings relative to one another than relative to the triazine ring leads to a weaker intramolecular interaction of the 'phenyl–phenyl' type compared with the 'phenyl–triazine ring' interaction. On this basis, the greater stability of the normal form of hexaphenylmelamine has been explained[104] by the significantly smallest steric strain in its molecule.

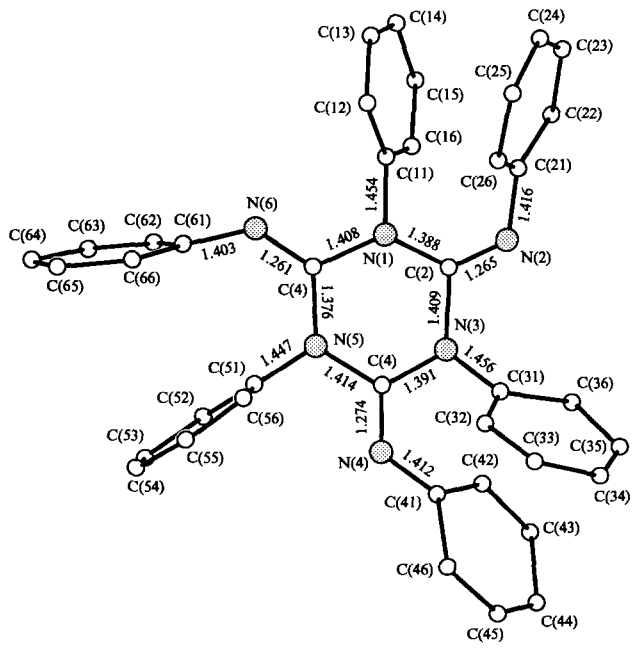


Figure 1. Projection of the hexaphenylisomelamine molecule onto the average plane of the heterocycle.

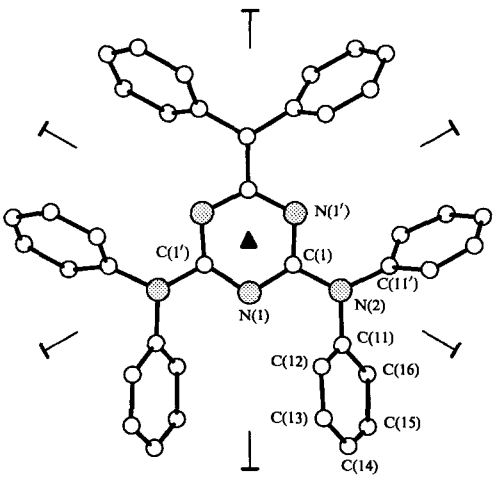


Figure 2. Projection of the hexaphenylmelamine molecule onto the plane perpendicular to the vertical symmetry axis.

Lebedev et al.[110] investigated the thermodynamic characteristics of a series of reactions modelling the processes occurring in the synthesis of oligocarbodiimides and structure formation in the latter.

The temperature dependence of the heat capacities of crystalline hexaphenylmelamine, hexaphenylisomelamine, as well as phenyl isocyanate and diphenylcarbodiimide in the crystalline, vitreous, supercooled liquid, and ordinary liquid states has been investigated in an adiabatic vacuum calorimeter in the temperature range 13.8–330 K with an accuracy to within ~0.3%; the enthalpies of combustion of the test substances at 298.15 K and a pressure of 101.325 kPa were investigated in an isothermal bomb calorimeter.

The functions $H^0(T)-H^0(0)$, $S^0(T)-S^0(0)$, and $G^0(T)-G^0(0)$ were calculated from the results in the temperature range 0–330 K; the zero point entropy and the difference between the zero point enthalpies of the vitreous and crystalline diphenylcarbodiimides and the thermochemical parameters of formation (ΔH_f^0, ΔS_f^0, ΔG_f^0) of the test substances were calculated at the standard temperature and pressure.

It was found that the enthalpy of the decarboxylation of phenyl isocyanate is comparatively small: $\Delta H_r = -(40.6 \pm 2.9)$ kJ mol^{-1}.

The enthalpies, entropies, and Gibbs free energies of the direct conversion of diphenylcarbodiimides into hexaphenylisomelamine and hexaphenylmelamine and of the isomerisation of hexaphenylisomelamine to the normal form are presented in Table 3.

Table 3. Thermodynamic parameters of the cyclotrimerisation of diphenylcarbodiimide to hexaphenylisomelamine and hexaphenylmelamine.[110]

T/K	Physical state of reactants	$-\Delta H^0$/ kJ mol^{-1}	$-\Delta S^0$/ J mol^{-1} K^{-1}	$-\Delta G^0$/ kJ mol^{-1}
	Cyclotrimerisation of compound **27** to **28**			
0	c, c	168.4	0	168.4
100	c, c	170.5	38.85	166.6
200	c, c	174.2	64.80	161.3
298.15	l, c	236.4	283.6	151.8
	Cyclotrimerisation of compound **27** to **29**			
0	c, c	326.6	0	326.6
100	c, c	329.7	61.76	323.5
200	c, c	334.5	94.42	315.6
298.15	l, c	397.4	316.3	303.1
	Isomerisation of compound **28** to **29**			
0	c, c	158.3	0	158.3
100	c, c	159.4	22.91	157.1
200	c, c	160.3	29.63	154.4
298.15	c, c	161.1	32.73	151.3

Note. The following designation of the states of the reactants has been adopted: l = liquid state, c = crystalline state.

In the temperature range 0–298 K, the cyclotrimerisation of the imide **30** and the isomerisation of compound **31** to **32** are thermodynamically allowed ($\Delta G < 0$). The upper limiting temperatures of these processes, found by extrapolation, exceed appreciably the temperatures of the onset of the thermal degradation of the reactants. The free energies of formation of compounds **31** and **32**, 1232.9 ± 7.4 and 1081.1 ± 13.1 kJ mol^{-1} respectively, indicate a greater thermodynamic stability of the latter compound, which confirms the conclusion that compound **31** may isomerise to compound **32** under kinetic conditions.[110]

Pankratov et al.[105] investigated in the temperature range 250–550 °C the thermal, thermooxidative, and thermohydrolytic stabilities of diphenylcarbodiimide **30**, the cyclic diphenylcarbodiimide dimer **24**, hexaphenylisomelamine **31**, and hexaphenylmelamine **32** — compounds which model the principal fragments of the network polymers based on oligo- and polycarbodiimides.

It was shown that, on thermolysis *in vacuo*, the stabilities of these compounds are approximately the same (the formation of the solid and liquid degradation products is observed at temperatures above 400 °C), but the thermooxidative stability of the products of the cyclotrimerisation of diphenylcarbodiimide, namely hexaphenylisomelamine and hexaphenylmelamine, is appreciably higher than that of the initial monomer. On the other hand, under the conditions of thermohydrolysis, the trimer **32** begins to decompose at 400 °C, which is 150 °C higher than the temperature of the decomposition of the N=C=N group in carbodiimide and the isomelamine ring.[105]

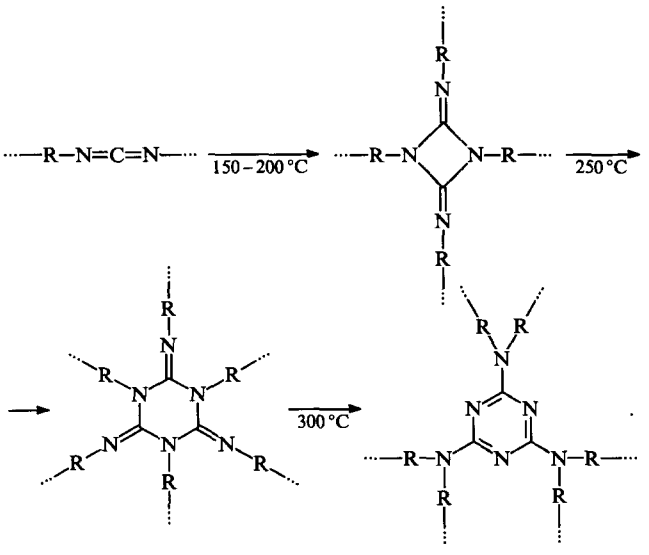
Taking into account the entire set of data concerning the chemical reactions of diphenylcarbodiimide under the influence of temperature, one may postulate that the reaction involving the formation of network polymers from oligocarbodiimides may involve, depending on the hardening conditions, the formation of three types of nodal fragments: uretediimine, isomelamine, and melamine fragments. Under these conditions, an increased number of melamine fragments in the structure of the cross-linked polymer should increase its thermal stability.

b. Polycyclisation of oligo- and poly-carbodiimides

There are literature data on the polycyclisation of polycarbodiimides. It has been stated in a number of studies[79,80,143,144] that the N=C=N groups of linear oligo- and poly-carbodiimides may polycyclise at elevated temperatures, but the structures formed have not been analysed.

In a number of studies[12,15,81,87,104,105,107–110,118,136,145–156] it was shown that, when aromatic oligocarbodiimides were heated, polymerisation took place with participation of the reactive N=C=N group and was accompanied by the loss of solubility and an increase in hardness and mechanical strength. At the same time, a weakening of the absorption band due to the carbodiimide groups in the range 2115–2145 cm^{-1} and the appearance of absorption bands in the range 1500–1700 cm^{-1}, corresponding to the vibrations of cyclic and dimeric (1690 cm^{-1}), isomelamine (1640 cm^{-1}), and n-melamine fragments (1530 cm^{-1}), were observed.

The influence of temperature and of process time on the degree and mode of isomerisation of oligocarbodiimides has been investigated by IR spectroscopy. A study was made of the dependence of the degree of conversion of the carbodiimide groups of the oligomers based on di(4-isocyanatophenyl)-methane and phenyl isocyanate (n = 25) on the duration of isothermal polymerisation at 150, 200, 250, and 300 °C. An increase in temperature from 150 to 300 °C induced an increase in the degree of conversion from 25%–30% to 70%–80%. The polymerisation temperature influenced significantly also the structure of the network polymers formed. Thus at 150–200 °C the principal reaction was cyclodimerisation, whilst on raising the temperature to 250 °C cyclotrimerisation of the carbodiimide groups predominated. At 300 °C and above, the appearance of an absorption band in the region of 1530 cm^{-1}, assigned to the vibrations of *sym*-triazine rings, was noted. Thus it is believed[81,105,107–109,118] that the following processes take place in the polymerisation of aromatic polycarbodiimides at different temperatures:



With increase in the temperature of the polymerisation of oligocarbodiimides, the degree of structure formation in the latter also increases. As a consequence of the preferential formation of the thermally more stable cyclotrimeric network nodes, the temperatures of the onset of mass loss and of the onset of deformation of the polymerisation products increase and there is also an increase in their hardness and mechanical strength (Table 4).

Table 4. Physicomechanical properties of the cross-linked polymers obtained by pressing the oligocarbodiimide (n = 25) based on di(4-isocyanatophenyl)methane and phenyl isocyanate (specific pressure 600 kgf cm^{-2}, material maintained for 1–3 min mm^{-1} at 25 °C).

Temperature/°C	Degree of structure formation (%)	Bending strength/ kgf mm^{-2}	Specific impact strength/ kJ m^{-2}	Brinell hardness/ kgf mm^{-2}
120	22–25	4.0–5.0	4–5	12.0–12.5
150	60–65	8.5–9.0	9–12	16.0–17.0
180	71–74	10.0–10.5	22–25	18.0–19.0
200	76–78	12.0–12.5	13–16	22.0–23.0
250	80–85	8.0–9.0	8–10	25.5–26.0
300	85–88	7.0–8.0	3–5	27.0–27.5

Analysis of the variation of the bending strength, specific impact strength, and Brinell hardness of the polymer specimens obtained by the compression pressing of the given oligomer under different conditions showed that an increase in the pressing temperature from 150 to 300 °C induces an increase in the Brinell hardness from 12–12.5 to 27–27.5 kgf mm^{-2}, while its specific impact strength and bending strength rise to a maximum for specimens structured at 180–200 °C and then fall again.

It has been shown [118] that the addition of 0.5 mass per cent of a cyclotrimerisation catalyst to oligocarbodiimides induced not only a 5%–10% increase in the degree of conversion of the carbodiimide group but also promoted the formation of isomelamine rings already at 150 °C. In the presence of catalysts, cyclotrimerisation becomes the dominant process at 220–250 °C. A further increase in the polymerisation temperature to 300 °C led to the formation of *sym*-triazine rings. Comparison of the IR spectra of the products of the purely thermal (at 300 °C) and catalytic polymerisation (at 250 °C) demonstrated a great similarity of their structures. In both cases, the polymer networks were constructed mainly from six-membered nitrogen-containing heterocycles.

A systematic survey has been made [107] of the thermal, thermooxidative, and thermohydrolytic stability of the structures of polycarbodiimides containing isomelamine and melamine fragments. A comparative study has also been made of linear polycarbodiimides based on 1,3-phenylene diisocyanate, 2,4-tolylene diisocyanate, and di(4-isocyanatophenyl)methane.

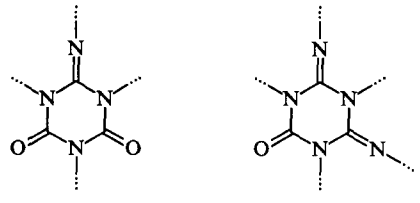
The kinetics of the degradation of these polymers have been investigated. [105, 107, 109] It was shown that the decomposition takes place as a first order reaction and obeys the Arrhenius equation. The rate constants and effective activation energies for the formation of gaseous degradation products as well as the effective activation energies for the decomposition reaction of the polymers were calculated.

Comparative study of the degradation reactions of polycarbodiimides *in vacuo* and in saturated water vapour demonstrated [107, 109] that the rate of decomposition of polycarbodiimides increases appreciably in a moist atmosphere. It was shown that the preliminary structure formation in the carbodiimide polymers *in vacuo* increases their resistance to thermal hydrolysis.

The principal types of oxidation reactions of polycarbodiimides have been established. They consist of the oxidation of the aliphatic and aromatic fragments of the macrochain and thermal structure formation involving the N=C=N groups.

Compounds containing melamine structures exhibit the highest thermo-oxidative stability. [105, 107, 109] The structure formation temperatures and times, ensuring an appreciable increase in the thermo-oxidative stability of network polymers relative to linear polycarbodiimides, have been determined. [107, 109]

There are literature data [144, 156] on the copolymerisation of diisocyanates with carbodiimides, which may result in the cocyclotrimerisation of the isocyanate and carbodiimide groups with formation of mixed cyclic trimers of the type



apart from the isocyanate and melamine rings.

3. Interaction of polycarbodiimides with various compounds

The existing numerous literature data concerning the interaction of polycarbodiimides with various compounds can be divided arbitrarily into two types.

1. Polymer-analogue reactions of polycarbodiimides based on the polymer chain of the polycarbodiimide, the reactive carbodiimide groups of which usually interact with monofunctional compounds of different nature.

2. Modification of various polymers by polycarbodiimides and monocarbodiimides. These reactions are no longer based on polycarbodiimides but on other polymers with other functional groups. In many cases, small amounts of added carbodiimides play the role of cross-linking agents, stabilisers, strengthening components, and agents imparting hydrophobic properties, i.e. substances which impart particularly valuable properties to the polymers.

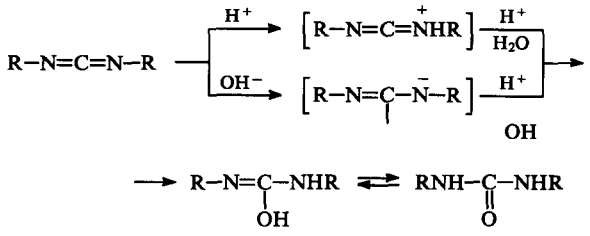
The chemical reactions of polycarbodiimides will be examined in this order in the present part of the review, resorting to examples of reactions of low-molecular-mass carbodiimides for a better understanding of the course of the reactions and of the structures of the products. There exist also other types of reactions of the carbodiimides. They have all been examined in detail in a series of thorough reviews on the chemistry of low-molecular-mass

carbodiimides.[18–25] However, they have not yet found applications in the chemistry of polycarbodiimides and we shall therefore not consider them.

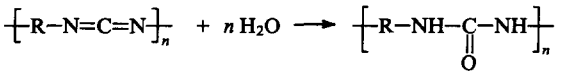
a. Polymer-analogue reactions of polycarbodiimides

The central carbon atom in the carbodiimide molecule exhibits striking electrophilic properties, so that nucleophilic addition reactions are the main type of reactions characteristic of carbodiimides.[18–25]

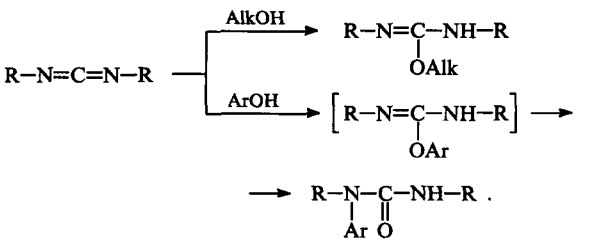
Hydrolysis of carbodiimides is a comparatively slow reaction catalysed by H^+ and OH^- ions.[157,158]



This reaction has been used to obtain polyureas.[69]



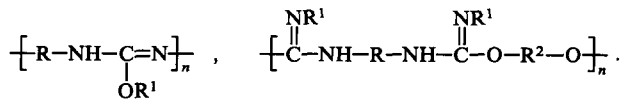
The interaction of carbodiimides with alcohols[159–162] results in the formation of *O*-alkylisoureas, whilst their interaction with phenols[163–165] affords *N*-phenylureas, which are formed via a stage involving the formation of *O*-arylisoureas.



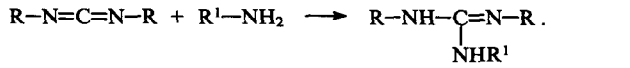
Reactions with certain acid phenols lead to the formation of *O*-phenylisourea derivatives.[166–171] They were obtained from pentachlorophenol[168,169] and 2,6-dichloronitrophenol.[172] It was postulated that the bulky *o*-chloro-substituents block the usual O→N shift in these compounds.[172]

However, picric acid reacts with carbodiimide to form *N*-arylurea, although the mechanism of this reaction apparently involves the formation of *O*-arylisourea as an intermediate.[173]

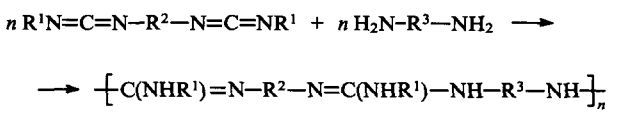
The application of this reaction to polymers[69,174] led to the formation of polyisoureas having the following structure:



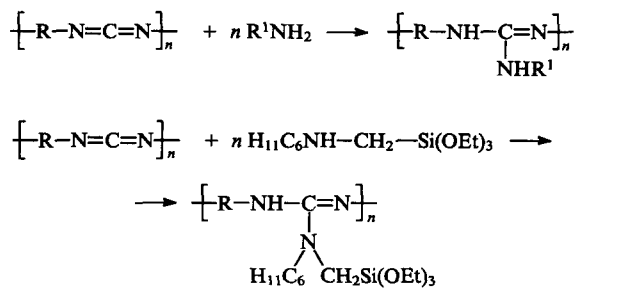
The study of the interaction of carbodiimides with amines showed that the products of this reaction are various guanidines.[175–177]



Polyguanidines were obtained as a result of the addition of biscarbodiimides to diamines.[178,179]

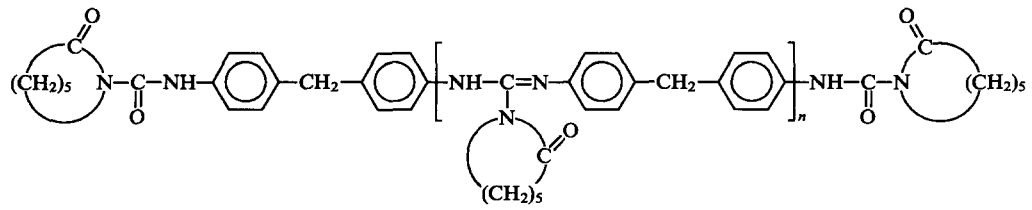


The synthesis of polyguanidines via the addition of primary and secondary amines to polycarbodiimides has also been described.[69,179]

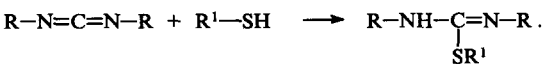


Interesting data have been obtained in a study of the interaction of ε-caprolactam with polycarbodiimides.[24] ε-Caprolactam is not only an excellent solvent for the sparingly soluble high-molecular-mass carbodiimides but it also adds quantitatively to polycarbodiimides on heating to 120 °C without the opening of the lactam ring (see the structure at the bottom of the page).

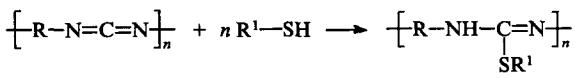
The adduct (n = 30) melted at 210–214 °C, i.e. at a temperature 70 °C lower than the melting point of the initial polycarbodiimide, and dissolved in dimethylformamide and *N*-methylpyrrolidinone. The polymers treated with ε-caprolactam had a wide molecular mass distribution with an average molecular mass of 11 000.

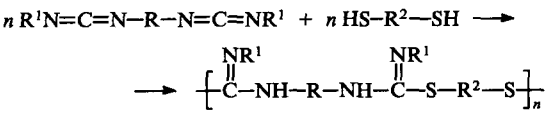


Mercaptans and thiophenols[180] interact with carbodiimide to form symmetrical alkyl(aryl)isothioureas.

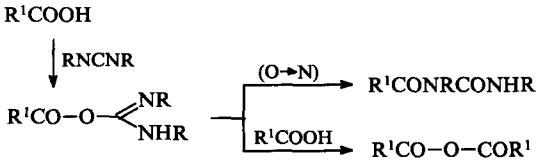


A similar reaction with polycarbodiimides[174,179] leads to the formation of polyisothioureas.

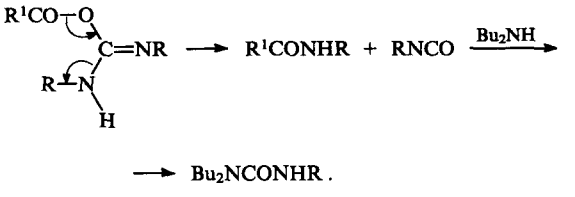




The interaction of carboxylic acids with carbodiimides has been investigated (together with the kinetics of such interaction) in fair detail.[181–190] The reactivity of the acids increases with their strength.[187] The reaction mechanism includes a stage involving the formation of anhydride via *O*-acylisourea and is complicated by the O→N shift.

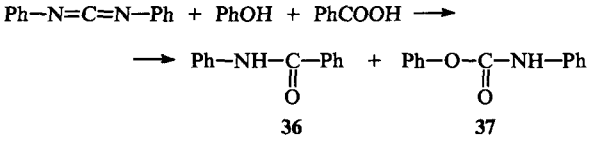


Another complication is the formation of the isocyanate (R—NCO) on decomposition of *O*-arylurea.[191]



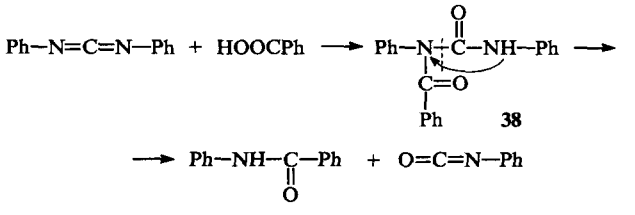
Di-n-butylamine was used as a 'trapping agent' for this isocyanate.[192]

The formation of isocyanates in the reactions of carbodiimides with carboxylic acids has been observed also in a study of the reaction of diphenylcarbodiimide with a mixture of benzoic acid and phenol.[193] Benzanilide **36** and phenylcarbamylate **37** were obtained as the products of this reaction.

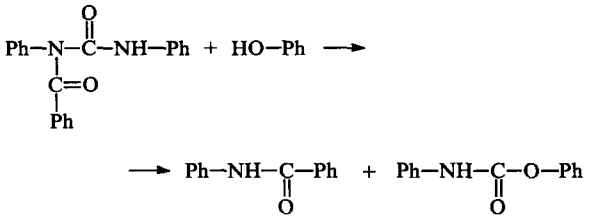


36 **37**

It was suggested that the anilide **36** is a product of the decomposition of *N*-benzoyl-*N,N'*-diphenylurea **38** formed in the first stage of the interaction of diphenylcarbodiimide with benzoic acid.

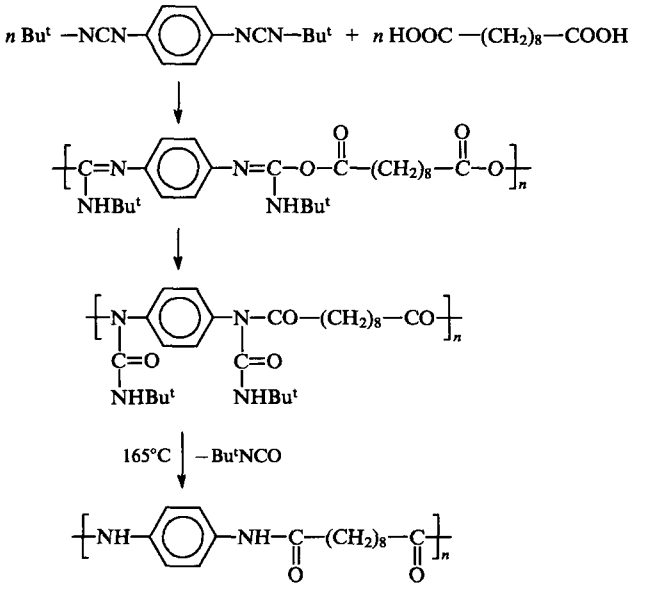


In order to test this hypothesis, compound **38** was allowed to react with phenol under the same conditions. This afforded benzanilide **36** in a satisfactory yield (80%).

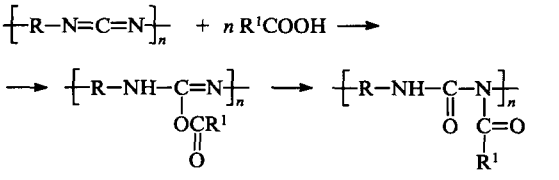


In addition, benzanilide **36** was isolated in 72% yield together with phenyl isocyanate from compound **38** itself on heating under the reaction conditions.

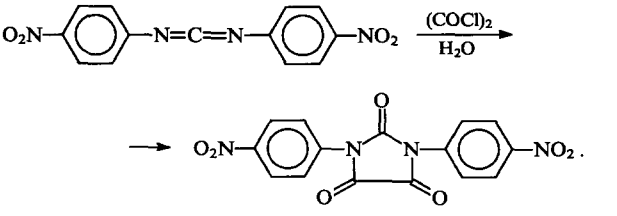
An interesting synthesis of the polymer has been achieved by the reaction of biscarbodiimide with dicarboxylic acids.[194] This synthesis was based on the use of the O→N shift of the acyl group.



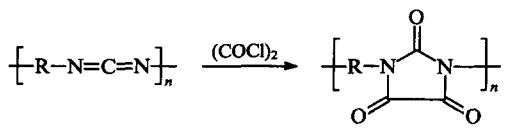
The interaction of monocarboxylic acids with polycarbodiimides leads to the formation of poly-*N*-acylurea, possibly via a stage involving the formation of poly-*O*-acylisourea.[195]



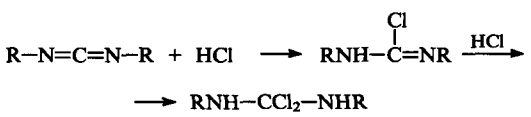
When arylcarbodiimides react with oxalyl chloride in the presence of water, the derivatives of parabanic acid are formed.[196]



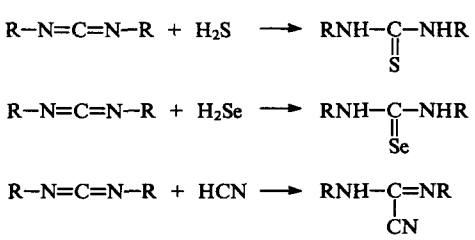
This reaction has been used [197] to obtain the highly thermally stable polyparabanic film by treating the polycarbodiimide film with oxalyl chloride.



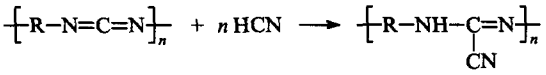
Dry hydrogen chloride reacts vigorously with carbodiimides with evolution of heat. Depending on the reactant ratio, one or two HCl molecules are added. [18]



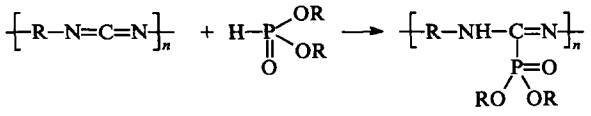
Carbodiimides react with weak acids, such as hydrogen sulfide [198] and hydrogen selenide, [199] to form the corresponding thio- and seleno-ureas, while the addition of hydrocyanic acid [200] leads to the formation of *N,N'*-dialkyl(aryl)-α-cyano-formamidines.



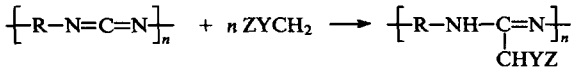
Among the reactions described above, that with hydrocyanic acid has been applied to polycarbodiimides, which resulted in the formation of polycyanoformamidines. [24]



Polymer-analogue reactions of polycarbodiimides involving the addition to the latter of dialkyl phosphites have also been carried out. [24]



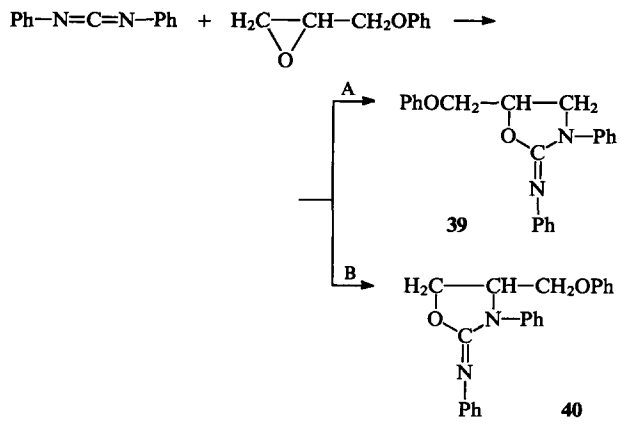
Polymers with formamidine fragments in the chain have been obtained by the addition of CH acids, for example malonic ester, to polycarbodiimides. [24]



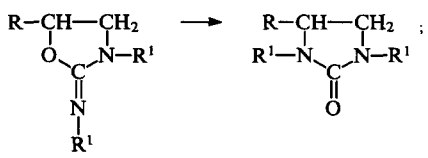
Z = COOEt, COMe;
Y = COOEt.

The interaction of the epoxide ring with the N=C=N groups of carbodiimides has been studied in detail on model and polymeric systems. [145–152] The model compounds employed were glycidyl phenyl ether and diphenylcarbodiimide. [145–147, 150–152]

Depending on the mode of opening of the epoxide ring, [12] there is a possibility of the formation of two isomeric structures: 5-phenoxymethyl-3-phenyl-2-*N*-phenyliminooxazolidine **39** and 4-phenoxymethyl-3-phenyl-2-*N*-phenylimidooxazolidine **40**.



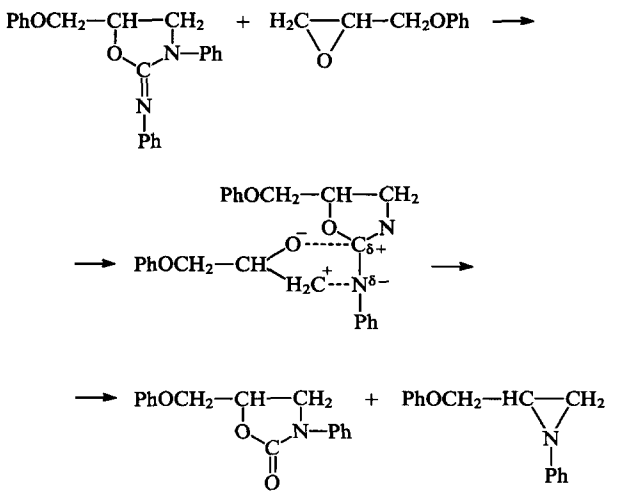
Analysis of the hydrolysis products as well as X-ray diffraction demonstrated [145, 147] that this reaction results in the formation of structure **39**. The X-ray diffraction data [147] made it possible to account for the absence of the isomerisation of compound **39** to the corresponding imidazolidinone, which is characteristic of iminooxazolidines with other substituents. [201, 202]



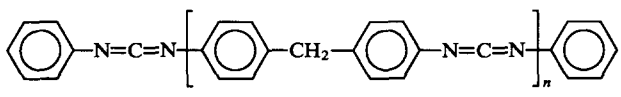
R = H, Ph; R^1 = Alk, Ph.

This is apparently associated with the fact that the phenoxymethyl substituent in structure **39** shields the ring oxygen atom, creating steric hindrance to the isomerisation process. [147]

It has been shown [150] that compound **39** interacts with an excess of glycidyl phenyl ether to form oxazolidinone.

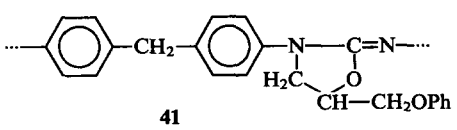


The interaction of oligocarbodiimides, synthesised from di(4-isocyanatophenyl)methane and phenyl isocyanate, i.e.

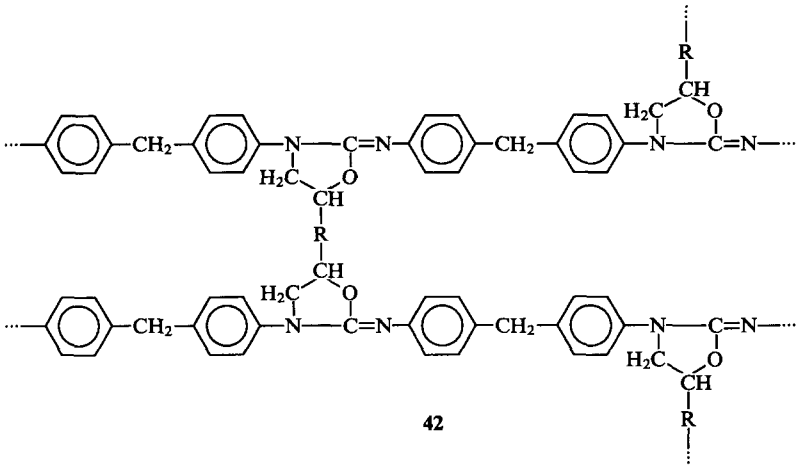


n = 30.

with glycidyl phenyl ether and the diglycidyl ether of di(hydroxyphenyl)propane has been investigated. The resulting polymeric structures are based on the fragments **41** and **42**. [146, 149]

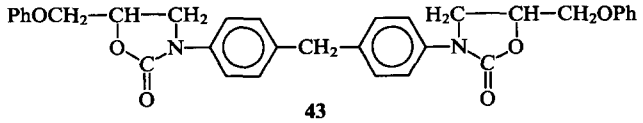


41



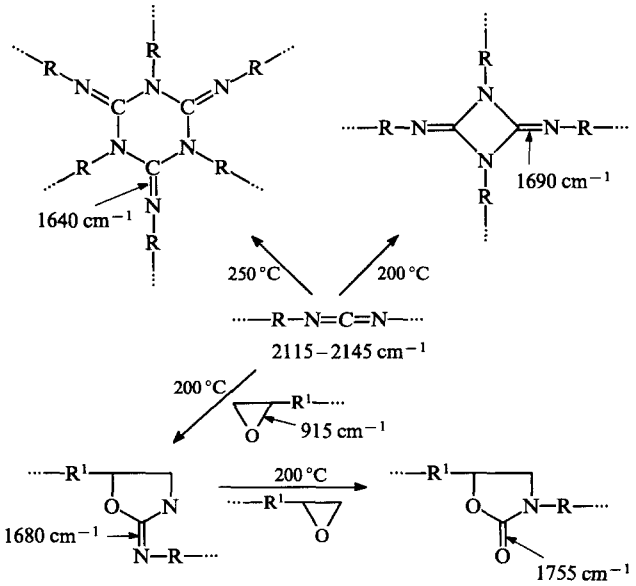
42

When an excess of glycidyl phenyl ether was used in the reaction with oligocarbodiimide,[146,149] bisoxazolidinone **43** was isolated, since iminooxazolidines decompose in an excess of the epoxide, which has been demonstrated in model reactions.[150]



43

The study[12,146,149] of the structures of network polymers obtained from oligocarbodiimides and oligoepoxides of different structure demonstrated the presence, together with imino-oxazolidine and other heterocyclic fragments, also of fragments obtained as a result of side reactions.

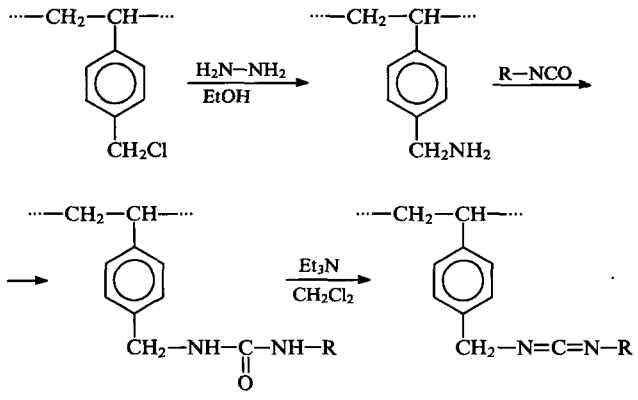


By altering the ratio of the carbodiimide and epoxide groups in the initial mixture of oligomers, the authors[12,146,149] regulated the content of heterocyclic fragments in the final product. In the presence of an excess of the oligocarbodiimide, urete diimine rings predominate in the structure, while at higher hardening temperatures (250 °C) the isomelamine groups predominate; in the presence of an excess of the epoxide component, the reaction involving the formation of iminooxazolidine and oxazolidine rings takes place preferentially.[12,146,149]

b. Modification of various polymers by mono- and polycarbodiimides

The development of new catalytic methods of synthesis of carbodiimides from available industrial isocyanates promoted the wide scale employment of mono- and poly-carbodiimides for the modification of various polymers.

Polystyrenes with carbodiimide side groups were obtained in this way. They were used subsequently as dehydrating agents.[203,204]

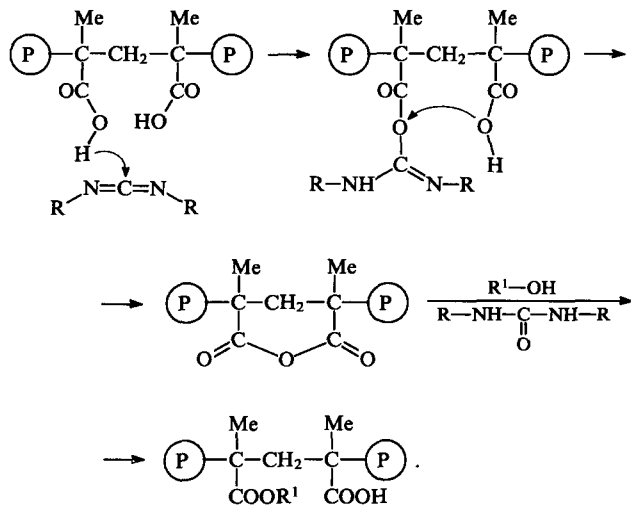


The cross-linking of butadiene–acrylonitrile copolymers, containing 0.09% of carboxy-groups, has been achieved.[205] The cross-linking agents were the bifunctional carbodiimides Ph–N=C=N–$(CH_2)_6$–N=C=N–Ph.

It has been shown in a patent[206] that hydroxyethylcellulose can be modified by means of dicyclohexylcarbodiimide in the presence of tetrafluoroboric acid with formation of a hydrophobic polymer containing *O*-alkylisourea units. Guanidine groups can also be introduced into the polymer under the conditions of such modification.[207]

When polyacrylic acids and polystyrenes with side carboxy-groups are treated with carbodiimides, polymers containing anhydride groups are formed.[208,209]

Syndiotactic polymeric methacrylic acid has been esterified by alcohols in the presence of carbodiimides and compounds with ester linkages have been obtained.[210–212] It has been suggested[210] that the formation of anhydride groups in accordance with the following scheme is an intermediate stage of the reaction:



Water-soluble carbodiimides have been used to bind ethyl glycinate to polyacrylic acid. It is suggested the reaction proceeds via the intermediate formation of a carboxylic acid anhydride.[208]

Scott et al.[209] investigated by IR spectroscopy the interaction between the carboxy-groups in cross-linked polystyrene in the presence of dicyclohexylcarbodiimide. It was postulated that *N*-acylurea groups are formed initially (absorption bands in the region of 1660 cm^{-1}) after which anhydride fragments appear, indicated by the presence of absorption bands at 1785 cm^{-1}.

Polymers containing amino- and carboxy-groups have been hardened with the aid of ditolylcarbodiimide.[213] The polymer films thus obtained are distinguished by improved physico-mechanical parameters.

Dicyclohexylcarbodiimide induces the formation of a sticky fire-resistant polyphosphoramide from diamines and inorganic phosphate.[214]

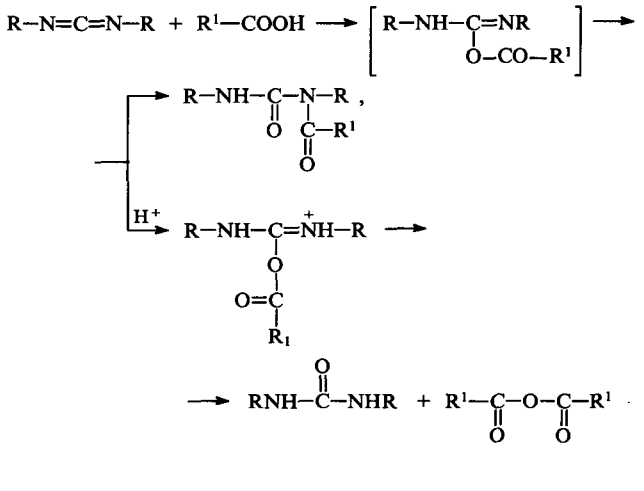
Carbodiimides have found extensive applications as hardening agents for gelatine.[215–227] The effect of carbodiimide consists in the binding of carboxy- and amino-groups in the gelatine chains, which leads to the cross-linking of the polymer.[227]

Polycarbodiimides have been used as dehydrating agents in the binding of peptides. Both linear polycarbodiimides and polymers containing carbodiimide groups in the side chain have been used for this purpose.[228–231]

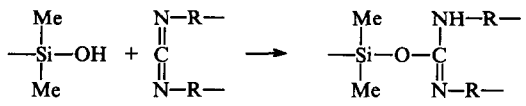
The storage time of liquid polyisocyanates can be increased by adding carbodiimides, which apparently remove water.[232–237]

Mono- and poly-carbodiimides are widely employed to prevent the hydrolysis of the ester bonds in polyesters[81,190,193,238–254] and as stabilising additives to polysiloxanes.[255,256]

It is believed[238] that the stabilising effect of carbodiimides is due to their interaction with the carboxy-groups of polymers.



It has been shown[255] that the siloxane linkages in polydimethylsiloxane are cleaved with formation of silanols at a temperature above 200–220 °C in the presence of water as well as alcohols and phenols. Such degradation leads to a decrease in the molecular mass of polydimethylsiloxane and hence to the loss of the initial physicomechanical parameters of the articles based on it. Piotrovskii and Metkin[255] state that the presence of polycarbodiimides during the hydrolysis of polydimethylsiloxanes may retard the decrease in the molecular mass of the latter as a consequence of the reaction of the silanol end groups with the polycarbodiimide.



V. Practical use of polycarbodiimides

The data presented above permit the conclusion that polycarbodiimides are promising polyfunctional thermoreactive compounds, which have found practical applications in various branches of technology, including the formation of highly heat-resistant and thermostable materials.

Polycarbodiimides are synthesised from available raw material in accordance with a technologically simple scheme. The high reactivity of carbodiimide groups permits both the thermal hardening of the polymers and different types of chemical modification of the latter. These positive qualities of polycarbodiimides promote their varied practical employment.

An important aspect of the practical use of polycarbodiimides is the formation on their basis of thermostable foams, the industrial manufacture of which has been initiated in recent years. They do not require the introduction of foam-forming agents (the role of which is assumed by the carbon dioxide evolved in the conversion of di- and poly-isocyanates into carbodiimides), their thermal stability is high, and they have effective physico-mechanical properties.[257–278]

It has been shown[259] that the modification of a polycarbodiimide composition by polyfunctional hydroxylated compounds makes it possible to economise on the carbodiimide formation catalyst, eliminates the differences between the technologies used for the preparation of foam polycarbodiimide and foam polyurethane, and increases the apparent density of the material. Under these conditions, 50% of the initial isocyanate groups of the polyisocyanate can be consumed on the formation of urethane fragments. The strength parameters of the resulting foam plastic are retained over a wide temperature range. For example, on raising the temperature to 127 °C, the relative elongation on rupture changes by only 50%.

It has been established[259] that foam polycarbodiimides, modified by urethane, exhibit a high fire resistance, have effective thermophysical parameters, and their water absorption capacity is low. This set of properties makes it possible to recommend them as insulating and constructional materials to be used at temperatures up to 200–250 °C.

Another possibility of modifying the polycarbodiimide structure arises from the simultaneous occurrence of the cyclotrimerisation of isocyanate groups with formation of isocyanurate fragments together with the polycarbodiimide.[259,269] They are highly fire-resistant: the mass loss does not exceed 15%–20% and the oxygen index is 29–32 in tests by the 'fire tube' method.[259]

A review has been devoted to fire-resistant carbodiimide foam plastics based on polyols derived from trichlorobutene oxides or epichlorohydrin.[279]

Organic[238,239,245–253,255,280–299] and organo-element[240,300–302] low-molecular-mass polycarbodiimides are used widely

as hydro- and thermo-stabilisers of polyesters,[238-254,280-284,290,291,295-298,300,301] polyurethanes,[299,300,301] polyamides,[280,292,298] polysiloxanes,[255,293] poly(vinyl chloride),[298,302] and other polymers.[46,53,59,70,72,215-237,285-288,294]

Aliphatic fluorocarbodiimides have been used to impart oil- and water-repelling properties to articles made from nylon and polyester [77] and also to impart these properties to leather. [77,303]

The addition of carbodiimides has made it possible to improve the adhesion of photographic emulsion to poly(ethylene terephthalate) carriers. The mechanism of the effect of carbodiimides apparently involves the formation of ester bonds. [304]

Mono- and poly-carbodiimides are used widely in the microencapsulation involved in the manufacture of pressure-sensitive copying paper. [305-307]

Organosilicon polycarbodiimides are stable in relation to irradiation, which makes it possible to employ them in various kinds of seals to be used under the conditions of intense irradiation. [25,86] Organotin carbodiimides are effective catalysts of the urethane formation reaction. [308,309] Thus $Bu_3N=C=NBu_3$ has been used as the catalyst for the preparation of film-forming polyurethane coatings based on organosilicon polyols and aliphatic isocyanates with the biurethane structure. [308]

Polycarbodiimides have been employed as nylon and polyester fibre and film strengthening agents. [310,311]

Polycarbodiimides have been used as composite binding materials: adhesives,[312-314] reinforced plastics,[15,82,197,315-317] compound materials,[12,79,146,149,156,232-237] electrically insulating materials,[153,155,318,319] and others. [77,320] This made it possible to obtain polymers with improved thermal and physicomechanical characteristics.

There is no doubt that further study of this promising class of polymers — organic and organoelement polycarbodiimides — will expand the scale of their practical applications‡.

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