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Polymerisation of Isocyanates

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The review deals with the present state of the problem of the ionisation of isocyanates: cyclic di- and trimerisation, homopolymerisation, and copolymerisation of isocyanates with other monomers. The mechanisms of the processes involving various catalytic systems are considered and the results of investigations of the polymerisation of isocyanates and their theoretical and practical importance are discussed.
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I. INTRODUCTION

The chemical reactions of isocyanates are extremely varied, but so far only some of them have been used industrially, in particular in polymer chemistry. They include mainly the reactions of isocyanates with nucleophilic agents containing a so called active (mobile) hydrogen atom (alcohols, diols, water, amines, etc.). The formation of urethanes has been most thoroughly investigated. They were studied and are still being studied systematically both on model and polymeric systems and the advances achieved in the understanding of the mechanism of these reactions have been described in a number of reviews [1-3]. Other reactions of isocyanates have been less thoroughly investigated, which to some extent restricts the scope of their useful applications.

Of the numerous reactions in which isocyanates are involved, cyclic dimerisation and trimerisation and also homopolymerisation of isocyanates and their copolymerisation with other monomers with formation of high-molecular-weight products are of significant interest for polymer chemistry. Several tens of publications dealing with the polymerisation of isocyanates have now appeared. They have not been discussed so far from a single standpoint and the brief reviews of the literature in certain papers [4,5] and monographs [1,6] on the dimerisation and trimerisation reactions of isocyanates, discovered as early as the past century by Hoffmann, cannot claim to give a complete coverage of the data. The possibility of the homopolymerisation of isocyanates with formation of high-molecular-weight products was first established by Shashoua in 1959 [17] and since then many papers dealing with a quantitative treatment of the polymerisation of isocyanates in the presence of various catalytic systems and with the search for new polymerisation initiators have been published.

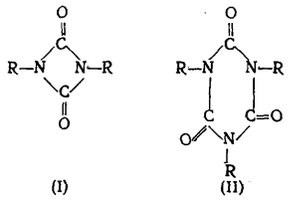
The fact that isocyanates are capable of entering into autocyclisation or polymerisation reactions with formation of linear high-molecular-weight products is not surprising if one bears in mind the electronic structure of the NCO group, which consists of a cumulative system of N=C and C=O double bonds. In this respect isocyanates are extremely similar to ketens $R_2C=C=O$, the capacity of which for cyclisation and homopolymerisation is well known [8].

The present review deals with almost all studies concerned in one way or another with the polymerisation reactions of isocyanates. We believe it reasonable to combine the discussion of the results of the study of the dimerisation and trimerisation of isocyanates, since in many cases they occur in the presence of the same or chemically similar catalysts, although there are a number of fundamental differences between these processes.

The problem of the homopolymerisation and of the copolymerisation of isocyanates with other monomers requires separate consideration. Together with its importance for polymer chemistry, the question of the possibility of the dissociation of the C=O bond in the NCO group in reactions involving the addition of nucleophilic agents to isocyanates, which has been frequently discussed (also by the authors of this review [2,3,9-11]) in connection with the mechanism of urethane formation, has a direct bearing on this problem.

2. CYCLIC DIMERISATION AND TRIMERISATION

The cyclic dimers (I) and trimers (II) of isocyanates are products of autocyclisation which takes place with dissociation of the N=C bonds:

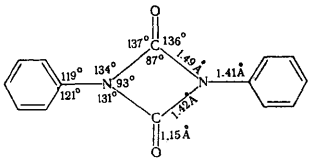


(I) (II)

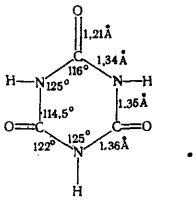
The dimers are a kind of symmetrical diketones (1,3-disubstituted uretidinediones); the trimers are derivatives of cyanuric acid (1,3,5-trisubstituted isocyanurates). The structures of isocyanate dimers and trimers have been demonstrated spectroscopically, by chemical analysis [4,12], and also by comparing the dimerisation and trimerisation products of isocyanates with products obtained by independent synthesis. For example, triphenyl isocyanurate was obtained from phenylcyanamide [13] and trimethyl isocyanurate was synthesised from cyanuric acid and diazomethane [14]. Compounds of type (II) were also

obtained by the condensation of cyanuric acid with oxiran, allyl chloroacetate, ethyl chloroacetate, and acrylonitrile [15].

The structure of the phenyl isocyanate dimer was established by X-ray diffraction [16]:



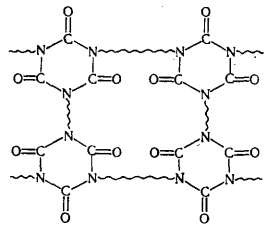
The central four-membered ring is planar. The length of the C–N bond corresponds approximately to its length in amides, for example in acetamide (1.426 Å), [17] and the length of the C–C bond in the aromatic ring differs only slightly from the usual length of this bond in benzene. There are no literature data on the structure of the trimers but some idea about it may be gained from an X-ray diffraction study of cyanuric acid [18]:



The six-membered ring of cyanuric acid is planar. One can hardly expect a significant change in the structure of the central six-membered ring on passing from cyanuric acid to isocyanurate. Before considering the dimerisation and trimerisation of isocyanates in the presence of various catalytic systems, we shall note why these reactions, which so far have been of purely academic interest (for the chemical properties of the NCO group), may be employed successfully in polymer chemistry for the synthesis of new materials.

The main procedure usually employed in the synthesis of structured (cross-linked) polyurethanes involves the introduction of various branching additives into the polymerising system. In the reactions of oligomeric polyesterdiols with di-isocyanates, triols are used for this purpose; polyesterpolyols or polyisocyanates containing more than two NCO groups per molecule can also serve as branching centres. The principal difficulty arising in the practical realisation of these processes reduces to the maintainance of an exact ratio of the concentrations of the NCO and OH groups and also involves the necessity to regulate with the aid of special catalytic additives or temperature conditions the ratio of the rates of all the reactions occurring in the system between NCO and OH groups, the reactivities of which are different depending on whether they are primary, secondary, or tertiary [1].

In the synthesis of structured polyurethanes by the trimerisation of isocyanates [19,20], a prepolymer containing terminal NCO groups, which are usually introduced by the reaction of a hydroxyl-containing polyol with di-isocyanates the NCO groups of which have fairly different reactivities (for example, 2,4-tolylene di-isocyanate), has been suggested as the starting material. In the presence of trimerisation catalysts, prepolymers with terminal NCO groups form a three-dimensional network:



In a system without hydroxy-groups, there is only one reaction—trimerisation of the isocyanate, the rate of which can be readily regulated by selecting an appropriate trimerisation catalyst.

Foams, varnishes, and polyaliphatic resins, which are hardened by the trimerisation of terminal NCO groups, are promising as regards technical applications. Polyisocyanurate resins formed, for example, by the cyclic polymerisation of aliphatic di-isocyanates, are distinguished by a high strength, thermal stability, and good optical properties and may be used to prepare plastics with improved optical transparency, which are used in aviation [20].

At the present time, the cyclic di- and trimerisation reactions of NCO groups in polymeric systems have been investigated inadequately, although some data concerning these reactions with participation of monomeric isocyanates are available. The catalytic systems used for this purpose and certain kinetic relations observed in the reactions are of main interest.

From the standpoint of the employment of the trimerisation reactions in polymer chemistry, it is significant that isocyanurates are much more thermostable than the usual polyurethanes. Thus the urethane chain breaks at a temperature as low as 150–200°C, while the thermal degradation of isocyanurates does not begin until 300°C. [21] Structured polymers, formed as a result of the trimerisation of NCO groups, are extremely rigid. In order to obtain fairly elastic materials, it is necessary to employ as the initial prepolymers oligomers the molecular weight of which is 3000–5000; plasticisers can also be employed.

The dimerisation of isocyanates is a reversible reaction, while the equilibrium in the trimerisation is almost completely displaced to the right. The equilibrium concentrations of the 2,4-tolylene di-isocyanate dimer are 8.5 and 7.1% respectively at 78° and 100°C. [22] When the temperature is reduced, there is a significant increase of the equilibrium concentration of the dimer and at 25° and 10° it amounts to as much as 71–74% and 90% respectively [4]. At 150–175°C the 2,4-tolylene di-isocyanate dimer is almost completely converted into the monomer.

Numerous catalytic systems for the dimerisation of isocyanates have been described [4–6]. The possibility of spontaneous non-catalytic dimerisation, which is extremely slow, has also been noted. Thus the equilibrium concentration of the 2,4-tolylene di-isocyanate dimer is reached at 78°C only after 1500 h. The activation energy for the spontaneous dimerisation of this isocyanate is 21 kcal mole^{-1}. [22] The best dimerisation catalysts are trialkylphosphines [23,24]; aryl- and alkylaryl-phosphines are less active.

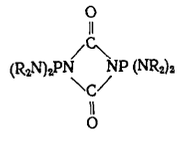
Isocyanates dimerise also in the presence of tertiary amines such as trialkylamines, pyridine, and its derivatives [4,5,25]. In recent years it was established that the

dimerisation of isocyanates also occurs in the presence of sodium benzoate [26], various organometallic compounds [6], and metal chelate complexes [6,27]. In most cases dimerisation is accompanied by trimerisation, but the above catalytic systems, particularly phosphines and tertiary amines, mainly promote the dimerisation reactions.

In the presence of iron acetylacetonate, the dimerisation of isocyanates is greatly accelerated compared with the non-catalytic process [27]. The reaction is then found to be of first order with respect to the catalyst and the activation energy is somewhat reduced, amounting to 19.5 kcal mole^{-1} for the dimerisation of 2,4-tolylene di-isocyanate.

The reasons for the catalytic activity of nucleophilic agents such as phosphines and amines should not be sought solely in their high basicity. For example, the basicities of dimethylphenylphosphine and dimethylaniline are similar, but the former is much more active as a dimerisation catalyst. Certain phosphines and their oxides catalyse the formation of carbodiimides R–N=C=N–R from isocyanates [28,29]. This reaction is a kind of dimerisation of RNCO with liberation of CO_2; $2RNCO \rightarrow R-N=C=N-R + CO_2$. The kinetics of the formation of carbodiimides in the presence of a number of catalytic systems have been investigated in fair detail [30,31].

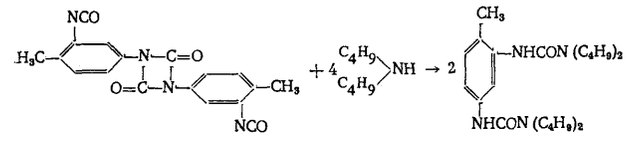
The capacity for dimerisation greatly depends on the structure of isocyanates. Aromatic isocyanates dimerise much more satisfactorily, owing to their lower electrophilicity. Teh dimerisation and trimerisation of acyl isocyanates RCONCO, in particular of benzoyl isocyanate and its methoxy-, chloro-, and nitro-derivatives in the presence of triethylamine, has also been described [32]. The formation of acyl isocyanate dimers and trimers is accompanied by side reactions involving the formation of cyclic products with breakdown of the C=O carbonyl bonds. Dimers of isocyanates derived from tervalent phosphorus acids with the general formula



were described recently [33]. Uretidinediones consisting of two different types of cyanates can be obtained [12].

The kinetics of the dimerisation reactions have been very little studied. One can only point to Davis's infrared spectroscopic investigations [22,27] of the solid-phase dimerisation of 2,4-tolylene di-isocyanate. The presence of an extremely intense band due to the stretching vibrations of the C=O group of the uretidinedione ring in the region of 1790 cm^{-1} makes it possible to identify the dimers readily and to investigate the kinetics of their formation from isocyanates. Downs and Haas [34,35] quote the infrared spectra of a number of dimers derived from phenyl isocyanate and the ^{19}F NMR spectra of isocyanate dimers with a fluorine substituent. Aryl isocyanate dimers melt in the range 160–200°C, depending on their structure [4].

The reactivity of the dimers is due to their capacity for dissociation with formation of the initial isocyanates and therefore their reactions with alcohols, water, and amines result in the formation of urethanes, ureas, and biurets respectively. Since the dimers may be formed spontaneously when isocyanates are stored, the problem of the correct chemical determination of the isocyanate number of monomers is important [36]. For example, it has been shown [37] that the reaction of the 2,4-tolylene di-isocyanate dimer with dibutylamine takes place according to the equation



and at a temperature as low as 50°C the conversion of NCO groups is in excess of 70%. The high reactivity of the dimer in the determination of the content of NCO groups in the monomer can lead to high isocyanate numbers. This factor has a direct bearing on the problem of finding the optimum NCO/OH ratio for the synthesis of polyurethanes from di-isocyanates and hydroxyl-containing polyester-polyols. The reactivity of the dimers in relation to the hydroxy-groups of alcohols and polyols is extremely low and a very long time is required for the urethane-formation reactions to occur even in pure alcohol. The reaction with acidic alcohols (for example with phenols) takes place to an appreciable degree only at 100–150°C.

There are no quantitative literature data on the reactivity of the dimers.

The trimerisation of isocyanates takes place in the presence of catalytic amounts of triethylphosphine [38], alkaline earth metal acetates, formates, and carbonates [13,39], metal naphthenates [40], aluminium chloride [41], oxalic acid [42], triethylamine [43], and iron, sodium, magnesium, mercury, nickel, copper, zinc, aluminium, tin, chromium, etc. salts soluble in organic solvents [44]. The brief review by Arnold et al. [4] of the early studies on the trimerisation contains a list of the catalytic systems for the trimerisation of isocyanates discovered up to 1957. In recent years there has been a considerable growth of interest in this reaction. New trimerisation catalysts have been discovered: sodium benzoate in dimethylformamide (DMF), [26,45] pyridine oxide [32], quaternary ammonium and phosphonium bases [46], metal alkoxides [47], tertiary amines [21], organic derivatives of quadrivalent tin [48], trialkylarsenic and arsenic oxides [49], metal acetylacetonates, and other complexes [27,50,51]. Trimers are also formed in the synthesis of urethanes in the presence of tertiary amines. Kogon showed [52] showed that, in the reaction of phenyl isocyanate with ethanol at 125°C in the presence of *N*-methylmorpholine, the phenyl isocyanate trimer is formed together with the urethane. It is interesting that the trimer appears only in systems containing an amine and an alcohol. In the presence of an amine and a urethane (ethyl carbamate) the trimerisation does not occur. In their attempt to prepare *N*-substituted oxazolidinones by the condensation of epoxides with isocyanates in the presence of pyridine, Jones and Savill [53] showed that the trimerisation reaction takes place vigorously under these conditions. Triphenyl isocyanurate was obtained in oxiran, propene, styrene, and epichlorohydrin solutions in the presence of traces of pyridine in a yield close to 100%. In the presence of oxides, quaternary ammonium bases also catalyse the trimerisation reaction, but much less effectively [53,54]. Subsequently these results served as a starting point in the search for new cocatalysts of the trimerisation in the presence of tertiary amines.

Isocyanate trimers are also formed in the high-temperature (230–250°C) condensation of bisurethanes of the type $RO-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_n-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-OR$ in the presence of titanium butoxide [55]. Isocyanate dimers and higher-molecular-weight products of different compositions are also formed

under these conditions. In those cases where the trimerisation and dimerisation of isocyanates take place simultaneously, the yield and rate of accumulation of each product vary significantly as a function of the conditions and the structure of the monomer. For example, in a study of the cyclic polymerisation of phenyl isocyanate in DMF at temperatures in the range 0–70°C under the influence of sodium benzoate, it was shown [26] that at 70°C the yield of the trimer was 50% of theoretical after 3 h and that of the dimer was less than 5%. At 0°C the content of the trimer fell to 30% and that of the dimer rose to 10%. At 30°C the ratio of the rates of dimerisation and trimerisation was 0.05%. [26] In the cyclic polymerisation of benzoyl isocyanate and its derivatives in the presence of tertiary amines and pyridine oxide, a significant change in the mode of reaction as a function of the structure of the isocyanate was established: at 50–80°C benzoyl isocyanate forms mainly the dimer under these conditions, while the less reactive *p*-methoxybenzoyl isocyanate yields the trimer—tribenzoyl isocyanurate [32].

Herbstman [49] made a detailed study of the trimerisation of isocyanates of different structures in the presence of a number of organic derivatives of antimony and arsenic. In the presence of 2 mole % of tri-n-butylarsenic and triisobutylarsenic oxides, phenyl isocyanate, and *m*-chlorophenyl isocyanate trimerise with a yield of 94–100% at room temperature over a period less than 1 h. The less reactive isocyanates *p*-$CH_3OC_6H_4NCO$ and C_2H_5NCO form trimers only on heating to 80°C with a yield of 95–97%. Isocyanates are very readily trimerised at low temperatures in the presence of catalytic amounts of tri-n-butylantimony diethoxide and diacetate. In the presence of triphenylarsenic oxide, even an inert monomer such as CH_3NCO trimerises in 15 min and *m*-chlorophenyl isocyanate forms under these conditions 30% of the trimer and 70% of carbodiimide. Antimony derivatives of the type $(t\text{-}C_4H_9)_5Sb$ and $(t\text{-}C_4H_9)_3SbCl_2$ do not catalyse the trimerisation process. It was established that tributylantimony oxide forms a stable complex with phenyl isocyanate, which is probably responsible for the catalysis [49]. The infrared spectrum of the complex has an intense C=O absorption band (1725 cm^{-1}); the N–H, N=C=O, and C=O bands of triphenyl isocyanurate (1705 cm^{-1}) are absent. A complex of the catalyst and triphenyl isocyanurate is not formed.

Organotin compounds are much less active as trimerisation catalysts. Bloodworth and Davies [48] showed that tributylmethoxytin $[(C_4H_9)_3SnOCH_3]$ and bistributyltin oxide $[(C_4H_9)_3Sn-O-Sn(C_4H_9)_3]$ react with isocyanates in equimolecular proportions to form 1:1 adducts. Under these conditions, the conversion of RNCO into the trimer is extremely slow.

There are no accurate quantitative literature data on the rates of trimerisation under the influence of organometallic compounds, with the exception of the results of a study of the trimerisation of 2,4-tolylene di-isocyanate in the presence of iron acetylacetonate [27]. The trimerisation reaction is of first order with respect to the catalyst, the catalytic effect of iron acetylacetonate in the trimerisation being more pronounced than in the dimerisation. Thus, 0.51 wt.% of the catalyst accelerates the solid-phase dimerisation reaction at 78°C by a factor of 60 and the trimerisation process by a factor of 200. The activation energy for spontaneous trimerisation in the absence of a catalyst is 16 kcal $mole^{-1}$ [22] and in the presence of iron acetylacetonate, 10.5 kcal $mole^{-1}$. [27] It is noteworthy that the cyclopolymerisation of isocyanates in the presence of iron acetylacetonate leads to an additional consumption of NCO groups in urethane formation, where iron acetylacetonate is frequently employed as a catalyst [56,57]. In the general case this is important, but comparison of the rate of urethane formation in the reaction between 2,4-tolylene di-isocyanate and the hydroxy-groups of a polyesterpolyol and the rate of the di- and trimerisation of this isocyanate in the presence of 0.5 wt.% of iron acetylacetonate shows that, while the first reaction is accelerated by a factor of approximately 50, [57] the consumption of NCO groups in the di- and trimerisation side reaction is only 0.1%, [27] i.e. it may be disregarded.

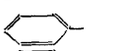
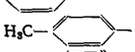
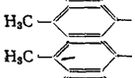
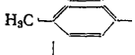
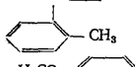
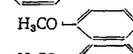
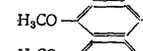
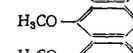
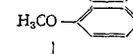
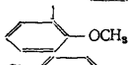
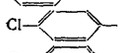
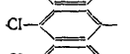
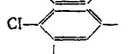
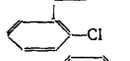
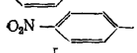
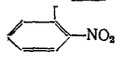
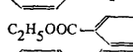
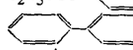
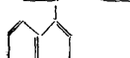
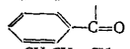
In the presence of organometallic compounds, isocyanate trimers do not form complexes with the catalyst [48,49], although isocyanurates are known to form readily molecular complexes even with the usual organic solvents, which can be identified spectroscopically [58]. The 1:1 complexes of a number of aryl isocyanurates with benzene, acetone, and DMF can be readily isolated in the form of colourless crystals. The infrared spectra of the complexes contains virtually the same bands as the spectrum of the free isocyanurate, but the relative intensity and position of the C=O band are altered. Table 1 lists the vibration frequencies of the C=O group in a number of isocyanurates and their complexes with solvents. Methanol, ether, and benzophenone do not form complexes with isocyanurates, but ethylene carbonate forms at 130°C a stable 1:1 complex with triphenyl isocyanurate having a molecular weight of 230, which corresponds to the formula $(C_6H_5NCO)_3.C_3H_4O_3$. [59] It is noteworthy that in the presence of traces of *N*-methylmorpholine the trimerisation of isocyanates is much faster when ethylene carbonate is introduced into the system as a cocatalyst, the reactivity of the resulting trimer bound in a complex with ethylene carbonate being higher in the reaction with primary amines than that of the free trimer [59].

The complexes of aryl isocyanurates with organic solvents are fairly stable at room temperature. *In vacuo* at 100–200°C the complexes decompose into the initial components. Aliphatic isocyanurates form complexes much less readily.

The mechanism and kinetics of the trimerisation of NCO groups can be inferred at the present time only from studies on trimerisation in the presence of tertiary amines and tertiary amine–cocatalyst catalytic systems [21,60,61]. As already stated, alkylene oxides are usually employed as cocatalysts; aldehydes, lactones, alkylene carbonates, and imines also exhibit a high cocatalytic activity. The trimerisation of NCO groups probably involves an anionic mechanism. In particular, this is indicated by data on the reactivity of aryl isocyanates in trimerisation: electron-accepting substituents accelerate trimerisation, while electron-donating substituents retard it (Table 2). [21] Interpretation of data for the relative reactivities of *meta*- and *para*-substituted phenyl isocyanates on the basis of the Hammett equation yields $\rho = 3.5$, which confirms the nucleophilic nature of the trimerisation of isocyanates. Steric factors play a significant role. This is reflected in a markedly lower reactivity of *ortho*-substituted aryl isocyanates (Table 2).

The trimerisation reaction in the presence of amines is significantly faster in polar media than in solvents with a low dielectric constant. Thus the relative reactivities of phenyl isocyanate in benzene ($D = 2.3$), chlorobenzene ($D = 5.7$), acetonitrile ($D = 37.5$), and dimethyl sulphoxide (DMSO) ($D = 45.0$) are 1.5, 2.4, 8.4, and 12.3 respectively [21]. The acceleration of the reaction in media with a high dielectric constant indicates a significant polarity of the transition complex in the trimerisation process.

Table 1. The position of the C=O bond in the spectra of isocyanurates and their complexes with organic solvents[58].

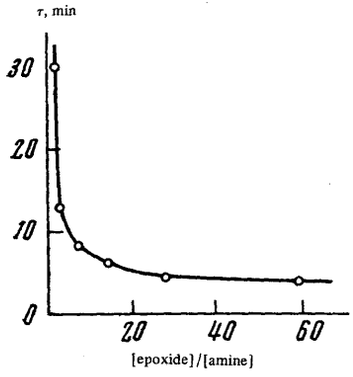
Group	M.p. of trimer, °C	Solvent	ν, cm^{-1}
	280	—	1695[52], 1710
	—	DMF	1700, 1670
	264	—	1765, 1715, 1690
	—	DMF	1700, 1675
	—	Benzene	1700
	—	Acetone	1700
	180	—	1695[52]
	260	—	1765, 1715, 1690
	—	DMF	1700, 1680
	—	Benzene	1700
	—	Acetone	1700
	261	—	1703[52]
	318	—	1770, 1715, 1690
	—	DMF	1700, 1670
	—	Acetone	1700
	201	—	1700[52]
	350	—	1765, 1715, 1685
	260	—	1703
	246	—	—
	374	—	1709[53]
	335	—	1713[53]
	344	—	1700[53]
	162 (decomp.)[32]	—	—
$-CH_2CH=CH_2$	19—22 [15]	—	—
$-CH_2COOC_2H_5$	71—78 [15]	—	—
$-CH_2CH_2CN$	228—230 [15]	—	—

The principal data on the catalytic activities of tertiary amines combined with cocatalysts of different types are quoted by Beitchman[60], who investigated the catalytic activities of a large number of tertiary amine–catalyst compositions by calorimetric methods from the rate of attainment of the maximum temperature rise in the system. It is striking that in the presence of triethylenediamine–alkylene oxide systems the kinetic curve is S-shaped. At the end of the induction period, the duration of which depends significantly on the concentration of both components of the catalytic system and the isocyanate, the reaction is of first order with respect to the monomer and 100% conversion is reached. The S-shape of the kinetic trimerisation curve is not a result of the autocatalytic effect of the reaction product: the shape of the kinetic curves remains unaltered when the dimer or trimer is introduced into the system before the start of the reaction.

The rate of the reaction catalysed by tertiary amine–alkylene oxide systems increases sharply with the [oxide]/[amine] ratio (see Figure) and reaches an approximately constant value from a ratio of about 30 : 1. It was shown subsequently[61] that the rate of trimerisation is proportional to the product of the concentrations of the components of the catalytic system; the presence of the induction period observed in the catalysis by the triethylenediamine–propylene oxide system[60] is not a general characteristic of reactions catalysed by tertiary amine–alkylene oxide systems

Table 2. Effect of the ring substituent in phenyl isocyanate on the reactivity of the monomers in the trimerisation reaction.

Substituent	σ	Relative reactivity
o-OC_2H_5		Very low
o-CH_3		0.06
m-CH_3	—0.07	1.92
p-CH_3	—0.17	3.95
o-Cl		0.09
H	0.00	10.0
m-Cl	0.37	70.0
p-Cl	0.23	128.0
p-Br	0.23	144.0
o-NO_2		20.5
m-NO_2	0.71	Very high
p-NO_2	0.78	Very high



Variation of the time of attainment of the maximum temperature rise in the system in the solid-phase trimerisation of tolylene di-isocyanate in the presence of the triethylenediamine–methyloxiran catalytic system with the [epoxide]/[amine] ratio (plotted on the basis of Beitchman's data[60]).

The catalytic activity of amines under the conditions of joint catalysis in the presence of oxides and other cocatalysts depends significantly on their structure but there is no direct relation with the basicity of the amines. Tertiary amines can be arranged in the following sequence in terms of their catalytic activity: triethylenediamine > triethylamine > *NNN'N'*-tetramethyl-1,3-butylenediamine > *N*-methylmorpholine > 2-methylimidazole[60].

It is also noteworthy that tertiary amines incorporating heterocycles with structures resembling that of the isocyanurate ring, for example the symmetrical *NN'N''*-tri-(dimethylaminopropyl)hexahydrotriazine or 2,4,6-tri-(dimethylaminomethyl)phenol, exhibit a high catalytic activity in the reaction [21]. One cannot rule out the possibility that, together with the basicity factor, the possibility of the coordination of the monomer to the catalyst plays a significant role in the mechanism of the catalysis by such amines. In order to elucidate this factor, detailed studies on the kinetics of the reaction and of the formation of a complex between the catalyst and the monomer are required.

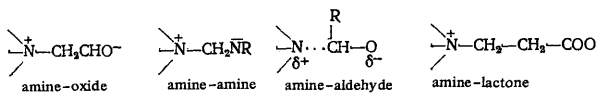
Table 3. Reactivities of olefin oxides, aldehydes, and imines as cocatalysts of the trimerisation of isocyanates (trimerisation of 2,4-tolylene di-isocyanate) in the solid phase (26–27°C; catalyst—0.0022 M triethylenediamine).

Cocatalyst*	τ, min**	t_{max}, °C***
Oxiran (0.020)	3.0	207
Methyloxiran (0.030)	6.0	202
Ethyloxiran (0.030)	7.7	—
Phenyloxiran (0.030)	49.0	164
Acetaldehyde (0.055)	16.0	73
Butyraldehyde (0.063)	45.0	110
Heptanal (0.056)	93.0	53
Trihydroxymethylenealdehyde (0.056)	67.0	128
Anisaldehyde (0.063)	242.0	70
Isodecanaldehyde (0.066)	128.0	87
Benzaldehyde (0.055)	69.0	82
1-Naphthaldehyde (0.056)	>76.0	—
Aziridine (0.0023)	3.0	164
N-Methylaziridine (0.0018)	<2.0	141
2-Methylaziridine (0.0018)	59.0	129

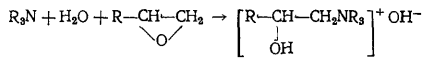
*The molar concentration is indicated in brackets.
**The time of attainment of the maximum temperature rise in the reaction characterising the relative reactivity of the cocatalyst.
***The maximum temperature rise in the reaction mass.

Table 3 shows that in the series of cocatalysts of different chemical types, alkylene oxides are the most effective. Although the times required for the attainment of the maximum temperature rise in the system cannot be strictly speaking regarded as criteria of catalytic activity, they can nevertheless be used for qualitative estimates.

The question of the nature of the active centre in the catalysis of the trimerisation by tertiary amine–cocatalyst systems is controversial. Despite the fact that there exists a possibility, in principle, of the opening of the epoxide, lactone, or imine rings in the presence of tertiary amines [62,63] and despite the significant polarisation of the carbonyl group when amines interact with aldehydes, the experimental proof of the involvement of zwitterions such as

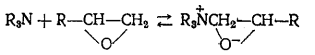


as active catalyst species in the reaction has not so far been found. One should also bear in mind the possibility of the formation in the amine–alkylene oxide systems of quaternary ammonium bases [64–66] as a result of the interaction with traces of water frequently present in solution in fairly large amounts (compared with the catalyst):



Definite information about the nature of the active centre in the reaction could be obtained from NMR data, but such experiments have not been performed. For catalytic systems of a similar chemical type (triethylphosphine–aldehyde and triethylphosphine–acrylonitrile) in the polymerisation of formaldehyde and acrylonitrile, it has been established by NMR [67,68] that the active species are zwitterions of the type $(C_2H_5)_3\overset{+}{P}-CH_2-\overline{O}$ and $(C_2H_5)_3\overset{+}{P}-CH_2-\underset{\displaystyle CN}{\overline{C}H}$, which interact with water or alcohol to form quaternary phosphonium compounds analogous to quaternary ammonium bases.

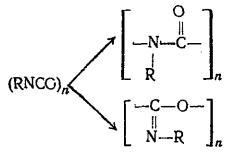
Petrov et al. [61] showed that, when dimethylbenzylamine and glycidyl phenyl ether are mixed together, the electrical conductivity of the mixture increases very rapidly, approximately by a factor of 200, and then remains unchanged for several hours. The opening of the epoxy-ring of glycidyl phenyl ether is much slower. The fact that in the trimerisation of NCO groups in the presence of this catalytic system an induction period is not observed, the electrical conductivity does not change after a sharp rise at the beginning of the reaction, and there is a linear relation between the rate of the process and the product of the concentrations of the components of the catalytic system enabled the authors to suggest the possibility of the formation of ion pairs at catalytically active species without the opening of the epoxy-ring:



The final determination of the nature of the active centre in the trimerisation reaction, the causes of ring closure in the trimer or dimer stage, and the relation between the yield of the trimer or dimer and the type of catalyst will be possible only as a result of a detailed investigation of the reaction kinetics under different conditions and a study of the processes occurring in the catalyst–cocatalyst interaction. These studies are directly related to the investigation of the polymerisation of isocyanates and the formation of high-molecular-weight products, since in both cases the process has an anionic mechanism consisting of a nucleophilic attack on the electrophilic carbon atom of the NCO group.

3. LINEAR HOMOPOLYMERISATION

In view of the structure of the isocyanate group, one must consider the possibility of the existence in a linear polyisocyanate or at least two types of homopolymers formed as a result of the dissociation of the N=C (III) or C=O bonds (IV) respectively:



(III)

(IV)

In the first case the macromolecular chain has the structure of an *N*-substituted polyamide and in the second it has

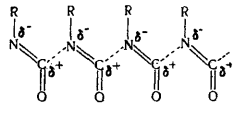
a polyacetal structure. A similar phenomenon is known in polymer chemistry. Thus, when ketens ($\begin{matrix}R\\R\end{matrix}\!\!>\!C=C=O$), which have a structure similar to that of isocyanates, are polymerised, both polyketones (polymerisation via the C=C bond) and polyacetals (polymerisation via the C=O bond) can be formed, depending on the conditions and the chemical nature of the catalyst. In a more general case, there is a possibility of the formation of polymers with alternating blocks or polymers having the ester structure[69,71]. In the homopolymerisation of isocyanates, it is very difficult to incorporate in the polymer chain structures (III) and (IV) simultaneously and can be achieved only in certain specific cases. Moreover, the isocyanate homopolymer with a purely polyacetal chain structure has not so far been obtained, although, as will be shown below, in certain copolymerisation reactions chain propagation takes place mainly as a result of the dissociation of the C=O bond.

Shashoua[7,72] and Natta[73] showed that in the presence of anionic catalysts the homopolymerisation of monoisocyanates involves the formation of high-molecular-weight ($M = 10^4-10^5$) polymers with a structure of type (III) in the main chain, i.e. substituted 1-nylons. The anionic polymerisation of about 30 different isocyanates has been studied[72]. The polymerisation takes place with a high yield in the presence of NaCN, sodionaphthalene, and sodiobenzophenone in DMF between $-20°$ and $-100°C$. The polymerisation of aliphatic and aromatic isocyanates has been investigated in the presence of ethyl-lithium, diethylberyllium, n-octylsodium, and lithium ethoxide in various solvents between $-60°$ and $-78°C$.[73]. It has been shown by X-ray diffraction that highly crystalline polymers are formed in all cases. Their infrared spectra have characteristic absorption bands in the region of 1700 cm^{-1} due to the presence of the C=O group. In the presence of cationic catalysts [$AlBr_3$ and $BF_3(C_2H_5)_2O$], amorphous polymers are formed in much lower yields[73]. In this case a mixed structure (III and IV) is probably formed in the main chain.

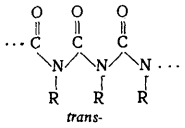
The yield and the molecular weight of the polymer obtained under the conditions of anionic polymerisation pass through a maximum as a function of catalyst and monomer concentrations in the mixture. When the temperature is reduced, the yield and molecular weight increase significantly[72].

The polymerisation of monoisocyanates under the influence of water-soluble initiators—alkalis and inorganic and organic acid salts in DMF at $-50°C$—has been described[50,74]. In the presence of alkalis the polymerisation is initiated by OH^- ions and in the presence of inorganic salts, by the acid anions. When alkali metal salts of carboxylic and dicarboxylic acids are used as the initiating system, the polymer yield is found to depend very markedly on the pK_a of the acid. In the presence of sodium salts of carboxylic acids with pK_a (in water) of the order of 1–3, there is hardly any polymerisation, while in the presence of salts formed by weaker acids (pK_a = 3–6) the yield of the polymer is 50–80%. With increase of the [H_2O]/[monomer] ratio, the yield and the molecular weight of the polymer fall.

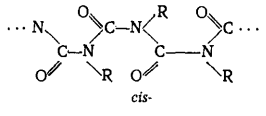
It has been established that the homopolymerisation of isocyanates occurs spontaneously on prolonged heating of the monomer[75] and also on radiation-chemical[76] and electrochemical initiation[77]. The pyrolysis of 2,4-tolylene di-isocyanate yielded linear dimers, trimers, heptamers, with the 1-nylon structure in the main chain[75]. It is interesting that radiation-induced polymerisation by γ-irradiation from cobalt-60 at temperatures between 20° and $-196°C$ can give high yields of isocyanate homopolymers, which, as in the presence of typical anionic catalysts, are formed by polyaddition with dissociation of the N=C double bond. Characteristic features of the radiation-induced polymerisation are the absence of an induction period, direct proportionality between the rate of polymerisation and the dose rate, and the acceleration of polymerisation at low temperatures when the polymer is in the solid state. It is also significant that in the presence of diphenylpicrylhydrazyl the yield of the polymer does not change, which shows that the radiation-induced polymerisation has a non-radical mechanism. The infrared spectra of polymers obtained in the liquid and solid phases are different and the stereoregularity of the "solid-phase" polymer is much higher. The structure of this polymer is identical with that of the polyisocyanates obtained by anionic polymerisation[72,73] and electrochemically[78]. It is suggested[77] that in the crystalline state the radiation-induced polymerisation takes place as a result of a cooperative interaction of the excited monomer molecule via the N=C bond:



Thus the available data show that in the anionic polymerisation of monoisocyanates the fundamental unit of the polymer chain is the amide group. Dielectric measurements[79] and also studies on the viscosity and sedimentation of poly(n-butyl isocyanate)[80] showed that the polyisocyanates obtained by polymerisation via the N=C bond are extremely rigid and probably have a helical conformation. X-ray diffraction data for poly(n-butyl isocyanate) obtained by the anionic polymerisation of n-butyl isocyanate confirmed the hypothesis of a helical configuration of the polymer chain[81]. The helix has a translation of 1.94 Å; the hexagonal unit cell parameters are a = 13.3 Å and c = 15.4 Å. It is suggested that the conformation of the elementary polyisocyanate unit is more consistent with the *cis*-structure than the *trans*-structure[81]:



trans-



cis-

The viscosity and light scattering data for solutions of poly(n-hexyl isocyanate) in tetrahydrofuran (THF) lead to an analogous conclusion[82].

Burchard[80] measured by sedimentation and diffusion methods the molecular weights of poly(n-butyl isocyanate) obtained by anionic polymerisation and established a relation between the viscosity of the polymer in benzene and tetrahydrofuran and the molecular weight:

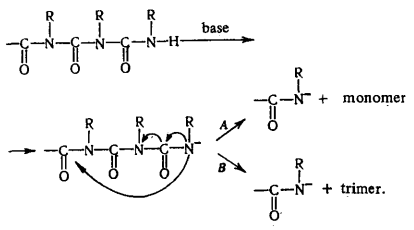
$$[\eta]_{THF} = 0{,}457 \cdot 10^{-3} \cdot M^{1{,}18}; \quad [\eta]_{benzene} = 1{,}10 \cdot 10^{-3} \cdot M^{1{,}11}.$$

A study of the dielectric properties of poly(n-butyl isocyanate) in benzene established a strong dependence of the relaxation time on the molecular weight[79]. Thus, when the molecular weight changes from 1.4×10^5 to 2.3×10^6, the change in τ_{obs} is from 1.6×10^{-6} to 5×10^{-3} s. Hence follows the conclusion of a broad

molecular weight distribution in the polymer. For example, it has been shown [79] by an independent determination of M_w and M_n for different polymer specimens obtained in toluene at −78°C in the presence of n-butyllithium that $M_w/M_n = 3.2-4.3$.

The amide structure of the polyisocyanates obtained on anionic polymerisation of monoisocyanates has been demonstrated by Iwakura et al. [83] by investigating the products and characteristics of the chemical degradation of the polymers in the presence of di-n-butylamine. The products of the reactions occurring at temperatures in the range 30−100°C over a period of several tens of hours are mainly cyclic trimers and the corresponding *NN*-di-n-butyl-*N'*-substituted ureas. The reaction is accelerated in the presence of bases and electron-donating solvents. In certain cases the formation of small amounts of free isocyanate (degradation of polymers formed from aryl isocyanates with electron-donating substituents in the ring) was observed.

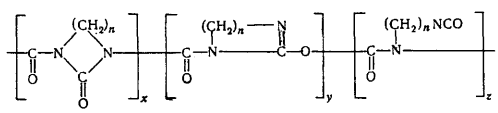
The mechanism of degradation in the presence of a base, the role of which reduces to the abstraction of a proton from the end of the polymer chain with formation of a macroanion, can be represented as follows:



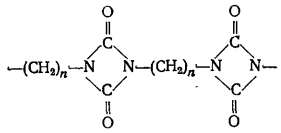
Depending on the chemical nature and conformation of the polymer chain, the reaction can proceed mainly via pathway *A* or *B* or via both simultaneously.

Interesting relations have been observed in the homopolymerisation of aliphatic isocyanates with different lengths of the methylene bridge between two NCO groups. Sections with a polyacetal chain structure were observed for the first time in the homopolymers formed from such monomers, which demonstrates the possibility of the homopolymerisation of isocyanates with dissocation of the C=O double bond. The polymerisation of aliphatic $\alpha\omega$-polymethylene di-isocyanates $OCN(CH_2)_nNCO$ with $n = 1-4$ in the presence of sodium cyanide in DMF at low temperatures was studied simultaneously by King [84] and Iwakura et al. [85] The polymers formed have an extremely high thermal stability and decompose as a rule above 350°C with the exception of the polymers formed from ethylene di-isocyanate. The polymers are soluble in hot sulphuric acid, *m*-cresol, DMSO, and ethylene carbonate.

It was shown that the infrared spectra of the polymers contain two types of absorption band due to the C=O group: at 1710−1770 and 1690 cm^{-1}. This demonstrates the simultaneous presence in the polymer of carbonyl groups in the ring (high frequencies) and in the main chain (low frequencies). On the basis of these data [84,85] and data obtained for the chemical degradation of the polymers [85], it was established that in the general case the polymer contains three types of structure:



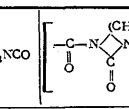
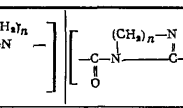
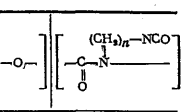
The quantitative proportions of various structures in the chain depend on the nature of the monomer, in particular on the length of the polymethylene chain (Table 4). Studies of the infrared spectra of the polymers led to the rejection of the "polydimeric" chain structure:



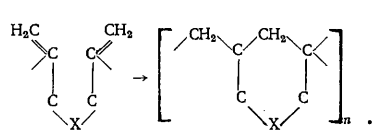
although the polymerisation of certain di-isocyanates did in fact occur in the presence of typical cyclic dimerisation catalysts, for example pyridine [85].

Linear cyclopolymerisation was also observed when cyclohexylene di-isocyanate, hydroxymethylene di-isocyanate, and 1,2,3-propylene tri-isocyanate were employed as monomers [84].

Table 4. The content of various structures in the chain of $\alpha\omega$-polymethylene di-isocyanate polymers (in %).

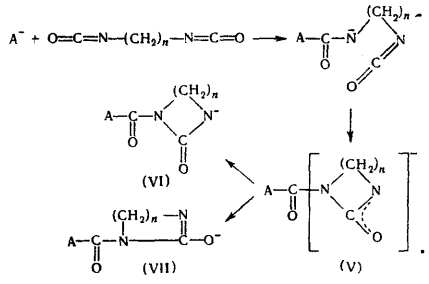
n in $OCN(CH_2)_nNCO$			
1	66	34	
2	0	100	0
3	76	24	0
4	40	60	0

Thus one may conclude that in the anionic polymerisation of $\alpha\omega$-polymethylene di-isocyanates the formation of linear polymers containing repeating cyclic units in the main chain takes place in accordance with alternating intermolecular and intramolecular chain propagation mechanisms. Ring formation of this kind in the growing main macromolecular chain is well known from studies on the polymerisation of dienes [86] and other bifunctional compounds containing ring double bonds [87]. The fundamental unit of such linear cyclopolymers can be readily represented if it is assumed that polymerisation requires the operation of alternating intramolecular and intermolecular chain propagation mechanisms:



In the linear cyclopolymerisation of di-isocyanates, initiation takes place as a result of the attack by the catalyst anion on the carbon atom in the isocyanate group located at one of the ends of the monomer. This results in the dissociation of the C=N bond, as in the anionic polymerisation of mono-isocyanates, with formation of 1-nylons. The second, intramolecular propagation stage may consist of the coordination of the nitrogen atom in the

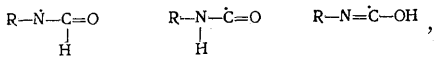
anion to the carbon atom of the second isocyanate group in the monomer with formation of a ring:



In the cyclic intermediate (V), the negative charge is in general delocalised between the nitrogen and oxygen atoms. Depending on the structure of the monomer, structure (VI) or (VII) is formed. Intermolecular chain propagation takes place via the attack by the macroanion on another monomer molecule at the N=C bond.

The question of the dissociation of the N=C or C=O bond in various reactions involving isocyanates is crucial to the chemistry of these compounds. Calculations on the distribution of electron density in the NCO group by the MO-LCAO method have shown that, depending on the structure of the isocyanate, electron density may be enhanced both at the nitrogen and at the oxygen atom [88]. The possibility of urethane formation and the hydrolysis of isocyanates via a stage involving the dissociation of the C=O bonds was recently demonstrated by oxygen isotope exchange [11]. There are no literature data permitting a comparison of the N=C and C=O bond energies in the N=C=O cumulative systems, but indirect information concerning a greater or lesser ease of dissociation of a particular bond may be obtained from the ESR spectra of the radicals formed on γ-irradiation of isocyanates and isothiocyanates and in their reactions with thermal hydrogen atoms [89].

Of the possible radicals formed in such reactions with various alkyl and aryl isocyanates involving the NCO group,

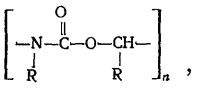


only the first two were detected in the system employed [89] and, depending on the structure of the isocyanate, a radical with an unpaired electron at the nitrogen or at the carbon atom was produced. However, these extremely useful data cannot be treated as proof of the impossibility of the dissociation of the C=O bond in nucleophilic reactions of isocyanates.

The relations in the polymerisation of isocyanates considered here and the data for this copolymerisation which are described below merely emphasise the earlier conclusion [10,11] that the reactions of isocyanates can involve the dissociation of both N=C and C=O bonds, which depends both on the structure of the monomer and hence on the distribution of electron density in the NCO group and on the mechanism of the process and reaction conditions.

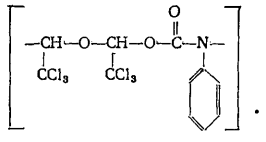
4. COPOLYMERISATION OF ISOCYANATES WITH OTHER MONOMERS

The majority of known copolymers of isocyanates have been obtained by their copolymerisation with aldehydes. Copolymers of formaldehyde with phenyl and alkyl isocyanates [90,91], of acetaldehyde with phenyl and ethyl isocyanates with tolylene di-isocyanate [92], and of butyraldehyde with phenyl isocyanate [92] have been described. Copolymers of phenyl isocyanate and *N*-sulphinyl isocyanate with chloral have also been obtained [93,94]. In most cases copolymerisation occurs in the presence of anionic initiators—sodium cyanide, sodionaphthalene, and fluorenylsodium, but in the copolymerisation of chloral the reaction occurs in the presence of tertiary amines [93] and organometallic complexes such as metal acetylacetonates [95,96]. It has been shown that the chemical nature of the monomers plays such a significant role in their capacity for copolymerisation that in some cases the reaction does not take place at all. Thus acetaldehyde, benzaldehyde, acrolein, and metacrolein do not copolymerise with phenyl isocyanate [92]; on the other hand, butyl isocyanate does not copolymerise with chloral [93]. The copolymers with aldehydes have a fundamental unit with a urethane structure:



(VIII)

i.e. in the copolymerisation the N=C bond of the isocyanate and the C=O bond of the aldehyde dissociate. The presence of the carbonyl group is evident from the infrared spectra (ν = 1725 cm^{-1}) of the copolymers. The molecular weight of the copolymers with chloral, obtained in the presence of triethylamine and triethylenediamine, is $(1-2) \times 10^4$. [93] The polymers have a high melting point (240–250°C) and are white powders readily soluble in benzene, chloroform, carbon tetrachloride, and other solvents. It has been shown by infrared spectroscopy and elemental analysis that the copolymers with chloral formed by anionic copolymerisation do not contain dimeric and n-meric isocyanate blocks, while two monomeric chloral units enter into the fundamental unit of the copolymer with phenyl isocyanate [92]:

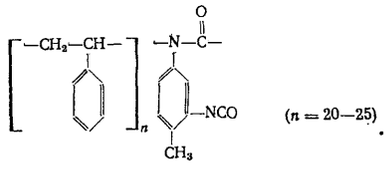


(IX)

In this copolymer the content of chloral corresponding to different monomer ratios (ranging from 3 : 1 to 1 : 3) varies from 62 to 75%. In the copolymer obtained in the presence of a tertiary amine, the content of chloral is 52–66%. The copolymerisation constants for the phenyl isocyanate–chloral system are respectively 0 and 0.4, [92] i.e. the phenyl isocyanate adds at a higher rate to the chloral than to the phenyl isocyanate molecule and conversely phenyl isocyanate is more reactive than chloral in relation to the anion of the latter. 1 : 1 copolymers of phenyl isocyanate and butyl isocyanate with chloral are formed in the presence of metal acetylacetonates, the catalytic activity of the latter depending on the nature of the metal and increasing in the sequence [96] Fe < Cu < Co < Ni. It has been shown by ultraviolet spectroscopy [96] that the formation of a complex by metal acetylacetonate with chloral is responsible for the initiation of polymerisation. The carbonyl group of chloral, inserted between the metal ion and the oxygen atom of acetylacetone, is polarised, which leads to an increase of the negative charge on the oxygen atom of chloral. Thus the copolymerisation has an anionic mechanism.

Isocyanates readily copolymerise with ketens; the mechanism of chain formation in this reaction does not show significant differences from the copolymerisation with aldehydes. At 0°C and room temperature in the presence of n-C_4H_9Li, LiOR, NaOR, and NaCN, diphenylketen and phenyl isocyanate form an alternating copolymer as a result of the dissociation of the C=O bonds of the keten and the C=N bonds of the isocyanate [97]. Block-copolymers containing several phenyl isocyanate units in succession are formed at lower temperature (−45°C).

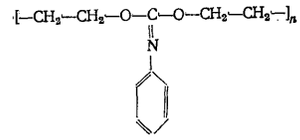
Copolymers of isocyanates with acrylonitrile and vinyl acetate [97], styrene, isoprene, methyl methacrylate, etc. [98-100] have been described. In the copolymerisation of tolylene di-isocyanate with styrene at 20−100°C in the presence of benzoyl peroxide and isopropylphenyl hydroperoxide initiators, the block copolymers (X) are formed:



(X)

The block-copolymerisation of vinyl monomers with butyl isocyanate and 2,4-tolylene di-isocyanate, which proceeds via a "live" polymerisation mechanism at low temperatures in the presence of n-C_4H_9Li in toluene–tetrahydrofuran mixtures has been studied in very great detail. The molecular weight distribution in the copolymers was investigated by gel chromatography: M_W/M_n is 1.14−1.17 in block-copolymers of styrene with butyl isocyanate and 1.5−1.6 in the copolymers of styrene, methyl methacrylate, and isoprene with tolylene di-isocyanate [99]. The di-isocyanate copolymers containing free NCO groups [copolymer (X)] are readily cross-linked by diols, water, and diamines and therefore are of significant practical interest. The trimerisation of the NCO groups can be used for the cross-linking of these copolymers.

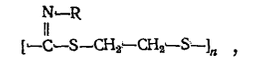
Studies on the copolymerisation of isocyanates with olefin oxides have a direct bearing on the possibility of the dissociation of the C=O bond in reactions involving isocyanates which we are considering. Furukawa and coworkers [101,102] were the first to establish that in the presence of triethylaluminium the monomers are copolymerised in the phenyl isocyanate–oxiran system together with the formation of polyoxiran. The copolymers contain acetal units in the main chain:



(XI)

The structure of the fundamental unit was demonstrated spectroscopically and by studying the hydrolysis products of the copolymers: one of the hydrolysis products of the copolymer (XI) is aniline. *N*-phenylmonoethanolamine should be formed in the hydrolysis of the copolymers formed by the addition of oxiran with dissociation of the N=C bond of the isocyanate.

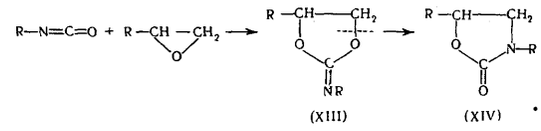
Subsequently a number of isothiocyanates were copolymerised with thi-iran in the presence of triethylamine [103], n-C_4H_9Li, and sodionaphthalene [104,105]. It was shown that the copolymerisation involves the formation of a polymer having the following structure:



(XII)

i.e. the addition of thi-iran to the isothiocyanate proceeds with dissociation of the C=S bond. The copolymerisation of thi-irans with isothiocyanates in the presence of typical anionic initiators involves the "live" polymerisation mechanism, which makes it possible to obtain block-copolymers of the required composition [105].

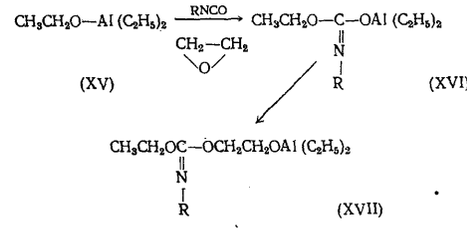
The very fact of polymerisation via the C=O and C=S bonds is not unexpected. Gulbins and Hamann [107] showed that the formation of the addition product (XIII) with dissociation of the C=O bond is an intermediate stage preceding the formation of 2-oxazolidinones (XIV) from epoxides and isocyanates:



(XIII) (XIV)

The conversion of compound (XIII) into 2-oxazolidinone (XIV) as a result of a rearrangement with opening of the dioxolan ring takes place at temperatures in the range 150−200°C and is catalysed by Lewis acids [108].

However, it has been shown [109,110] that compounds of type (XIII) and (XIV) are not intermediates in the copolymerisation of isocyanates with epoxy-compounds in the presence of triethylaluminium. The copolymerisation has a coordination-anionic mechanism with alternating insertion of the monomers in the Al−O bond of the diethylaluminium monoalkoxide (XV) and compound (XVI) being formed:



(XV) (XVI)

(XVII)

The structure of the intermediate (XVI) was established by infrared and NMR spectroscopy.

The data discussed above show that, despite the considerable number of studies concerned in some way with the problem of the polymerisation of isocyanates, the question of the mechanism of the processes involving various catalytic systems is still far from being finally elucidated. The limited number and in some cases the total absence of quantitative kinetic studies hinders greatly both the interpretation of the results and the possibility of a deliberate regulation of the rates of the processes and of the composition of the polymers formed. Much still remains to be done in the field of isocyanate polymerisation and one of the aims of the present review was to draw the attention of investigators to this interesting problem, which is important from the practical point of view.

After the manuscript had been sent to the editors, a number of studies with data on new catalytic systems and on the trimerisation [111-113], polymerisation [112,113], and copolymerisation of isocyanates with various monomers [114-121], as well as data on the thermal degradation of polymers with isocyanurate rings in the chain [122] and detailed studies on the properties and structures of polyisocyanates in solution [123-125] were published.

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