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Heterocyclic bifunctional monomers in the synthesis of polymers

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ABSTRACT. One of the variations of activated polycondensation, the "active ring" method is reviewed. The method consists essentially of the reaction of *bis*- and polyfunctional nucleophiles with monomers containing various heterocycles (three-, four-, five- and six-membered rings) as the electrophilic functional groups. Polyaddition reactions in which the heterocycle is opened are examined. It is demonstrated that many of the discussed reactions are promising for the synthesis of functionalised polymers that are often unattainable using traditional polycondensation methods.

The bibliography includes 139 references.

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I. Introduction

Heterochain polymers traditionally are synthesised using high-temperature or low-temperature polycondensations. The latter is based on the use of activated monomers such as dichloroanhydrides, *bis*-chloroformates and *bis*-carbamoylchlorides, diisocyanates, etc.[1–5]

Recently new polycondensation methods based on novel methods of activating monomers and arbitrarily called "activated polycondensation" have become widespread. Five principal directions have been defined.[6] Two of the methods of activated polycondensation, "direct polycondensation"[7,8] and the "leaving group" method,[6] have been analysed in the cited references.

The present review treats a third type of activated polycondensation, the "active ring" method.

The method consists essentially of the polycondensation of heterocyclic compounds of increased reactivity due to intramolecular electronic effects or strain in the ring with nucleophiles. During the reaction the ring opens†, often under mild conditions. The resulting polymers are difficult to produce using other polycondensation methods. This is especially true of functionalised polymers. The review does not include reactions involving dianhydrides of tetracarboxylic acids, upon which the synthesis of thermally resistant polyimides is based. These have been thoroughly discussed in numerous monographs and reviews (for example, see Refs. 9–11). Reactions occurring without opening of the heterocycle, for example, copolymerisation (also a polyaddition process) or polycondensation involving the heterocycle, also are not included. These have been reviewed before.[12]

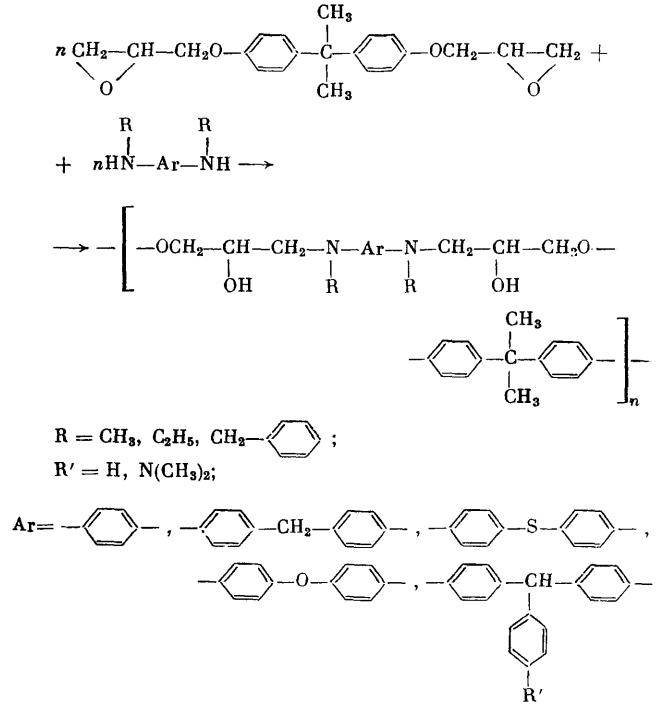
In the present review, we attempted to correlate examples of the use of various bifunctional heterocyclic monomers in polyaddition reactions with ring opening[12] and to describe some of the properties of the polymers formed.

Three-, four-, five- and six-membered heterocycles containing O, N, or O (more rarely S) and N together are discussed separately.

II. Three-membered heterocycles

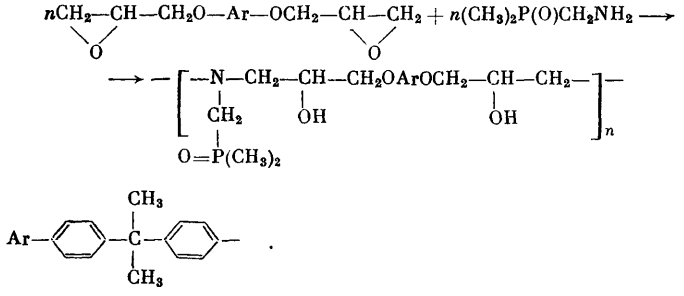
1. *bis*-Epoxides. The role of epoxides in the chemistry of high-molecular-weight polymers is well known. The present review is not concerned with the widespread processes that use epoxide resins. Only certain comparatively new polymer-synthesis reactions involving monomers containing oxirane rings are discussed.

It is known that diepoxides react with diamines by forming crosslinked polymers.[13,14] Hoerhold, et al.[15,16] successfully synthesised linear polymers ($M_n = 8-18 \times 10^3$) of polyamines with hydroxyl side groups by reacting *bis*-glycidyl ethers of *bis*-phenol-A with *N,N'*-alkyl-substituted aromatic diamines:

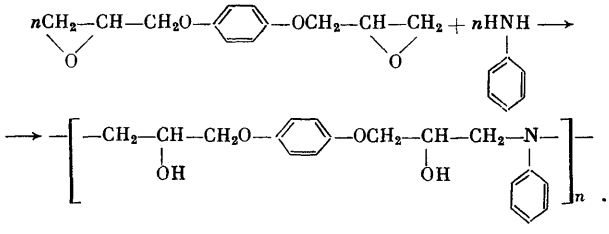


†Such polymerisation processes can be categorised as "multiple addition reactions with ring opening".

Using a phosphorus-containing primary monoamine as the monomer, linear polyaminohydroxy-ethers (M_n = 12.2 × 10^3) with increased fire-resistant properties are produced:[17]



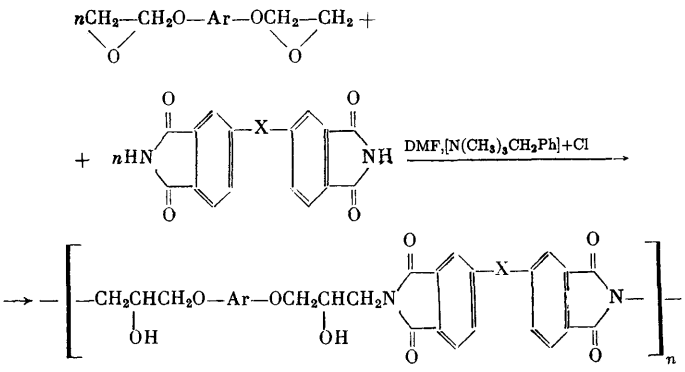
Iwakura, et al.[18] effected an essentially similar reaction by using aniline as the nucleophilic monomer:

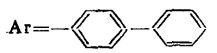


This resulted in linear polyhydroxyaminoethers capable of forming fibres.

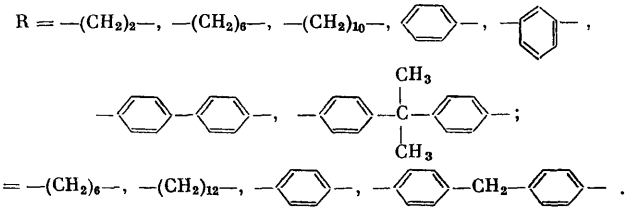
An interesting feature of the above reactions is that the primary amines exhibit a practical functionality (Φ_{pr}) of two.[19]

The reaction of bisimides with diepoxides[20] produces linear polyhydroxyalkylimides that are soluble in polar aprotic solvents (η_{inh} = 0.10–0.19 dl g^{-1}):

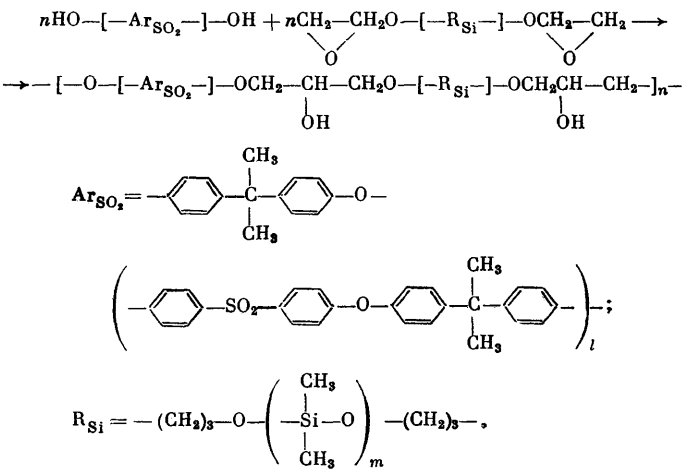




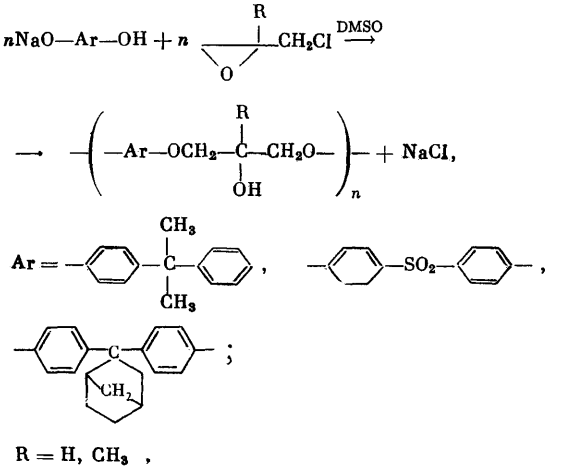
X = CO, COOROCO, CONHR'NHCO;



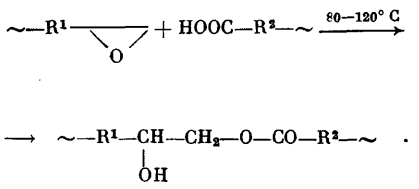
Having investigated in detail the model reaction between phenol and the epoxide ring in a melt,[21] Marechal, et al.[22] successfully used it to synthesise simple polyethers containing hydroxyls, in particular, block polyethers, through the reaction of α,ω-diphenyloligosulphones with α,ω-diepoxyoligosiloxanes:



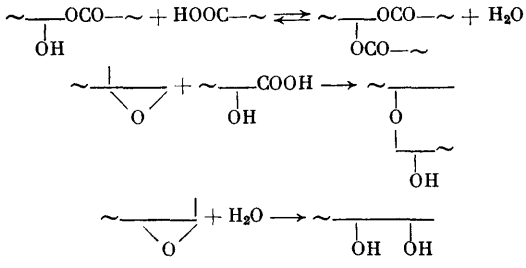
Rokicki and Kuran[23] prepared simple polyethers containing hydroxyls in one step without preliminary synthesis of the *bis*-glycidyl ethers:



Based on a detailed study of the reaction of epoxides with carboxylic acids, linear polyesters could be synthesised according to the scheme:[24–26]



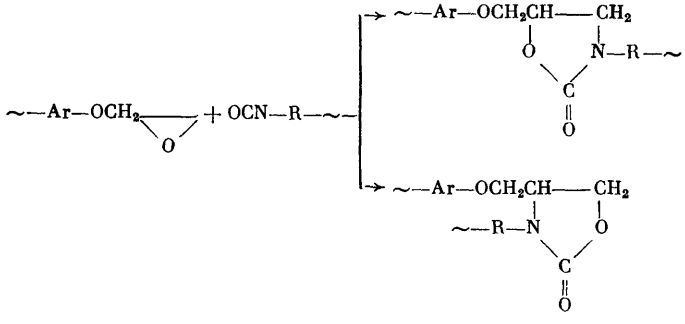
It was found that side reactions including those involving side hydroxyl groups that lead to crosslinked polymers occur only at higher temperatures.



Use of Cr^{III} diisopropylsalicylate instead of tertiary amines as catalyst helps to suppress these undesired reactions.

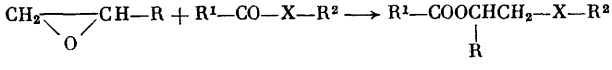
The prepared polyesters with side hydroxyl groups are capable of further polymeric conversions and can have practical application, for example, as biodegradable carriers of bioactive substances etc.

Frisch, et al.[27,28] established that the reaction of *bis*-glycidyl ethers with diisocyanates can be used to synthesise polyoxazolidones. Two isomeric rings are formed, the ratio of which depends on the reaction temperature:



The synthesis of polyoxazolidones through reaction of epoxides with isocyanates are examined in greater detail in a review.[29]

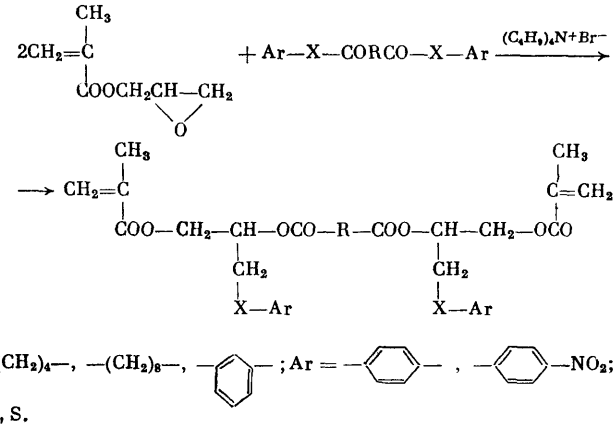
Korshak, et al.[29–32] discovered an interesting insertion reaction of oxirane rings into the bond to the heteroatom (esters and amides):



X = O, NH.

These reactions were used to modify the properties of polyesters and polyamides by reacting them with epoxide resins.

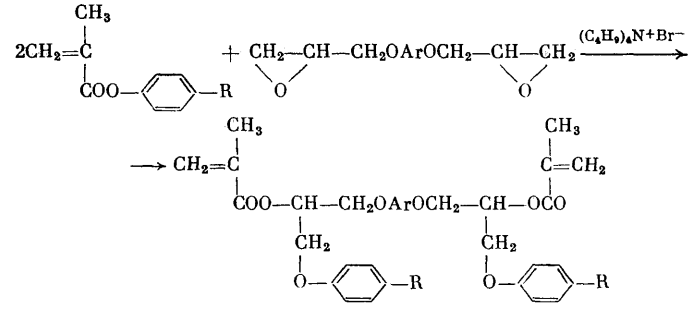
Nishikubo, et al.[33,34] also found that glycidyl ethers react with activated diesters of dicarboxylic acids according to the insertion scheme mentioned above. The reaction occurs under conditions enabling the readily polymerising double bonds to be preserved:

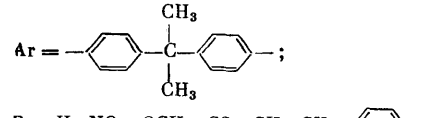


R = $-(CH_2)_4-$, $-(CH_2)_8-$, ; Ar = ,

X = O, S.

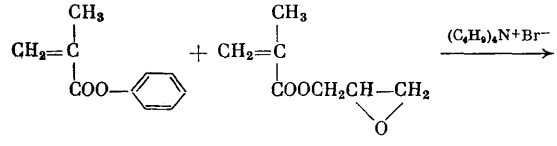
Bifunctional unsaturated monomers were also obtained by an alternative scheme:

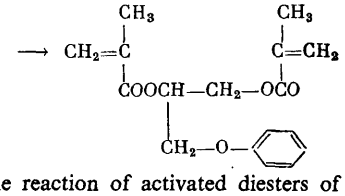




R = H, NO_2, OCH_3, CO—CH=CH—  etc.

or

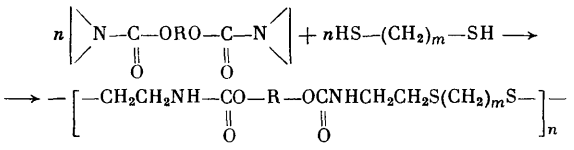




The reaction of activated diesters of dicarboxylic acids with the oxirane ring that occurs at elevated temperatures was also used to harden epoxide resins.[34]

The insertion reactions described above can apparently be used to synthesise linear polymers, converting them into bifunctional compounds. Such processes would be promising for preparation of functionalised polymers.

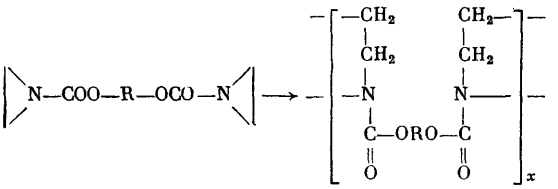
2. Aziridine derivatives. Iwakura, et al.[18,35] already at the start of the 1960s proposed an original synthesis of high-molecular-weight ($[\eta] \leqslant 1.4$ dl g^{-1}) polyurethane sulphides. The method consists essentially of alkylation of dimercaptans with polymethylene-*bis*-(*N,N*-ethyleneurethanes) in DMF at 75–120 °C in the presence of triethylamine:



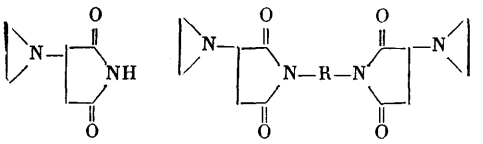
where R = $-(CH_2)_{4-6}$, *trans*-1,4-cyclohexyl, and *trans*-hexahydro-1,4-xylenyl.

It was found that the polyurethanesulphides prepared by this polyaddition scheme are slightly more heat resistant than analogous polymers synthesised by interphase polycondensation of the corresponding *bis*-chloroformates with polymethylene-*bis*-(β-aminoethylthioethers). The other characteristics of the polymers are completely identical.[35]

At elevated temperatures (in the absence of the dimercaptan), *bis*-(*N,N*-ethyleneurethanes) polymerise with ring opening to form polymers that are insoluble in organic solvents:



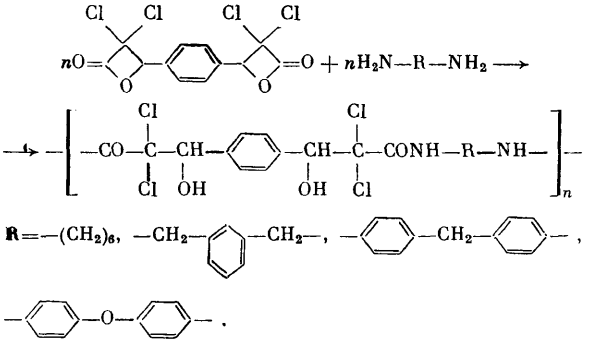
The molecules 3-(1-aziridinyl)succinimide and *N,N'*-alkylene-*bis*-(1-aziridinyl)succinimides were also suggested as monomers.[36]



These compounds polymerise at 125 °C in the melt with opening of the imide and imine rings to form crosslinked polymers. Under the appropriate conditions they can be used in linear polycondensation.

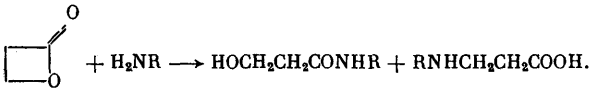
III. Four-membered heterocycles

***bis*-β-Lactones.** It is known that β-lactones are highly reactive toward nucleophiles due to strain in the four-membered ring.[37] This feature was successfully used by Ueda, et al.[38] to synthesise high-molecular-weight polyamides containing hydroxyls ($\eta_{inh} \leqslant 1.12$ dl g^{-1}) through reaction of 3,3'-*p*-phenylene-*bis*-(2,2-dichloro-β-propiolactone) with diamines:



It is noteworthy that the high-molecular-weight polyamides are formed even with aromatic diamines under mild conditions (20 °C in nonpolar dioxane, although the reaction does indeed take 12 days).

It was found that aminolysis of this *bis*-β-lactone occurs exclusively with cleavage of the O-acyl bond whereas the O-alkyl bond also breaks in the unsubstituted propiolactone to form the *N*-substituted β-aminoacid:

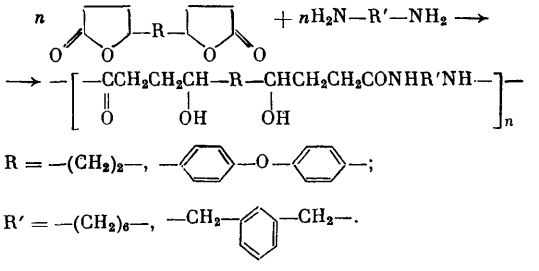


Apparently the two Cl atoms affect the *bis*-lactone and additionally activate the carboyl group.

IV. Five-membered heterocycles

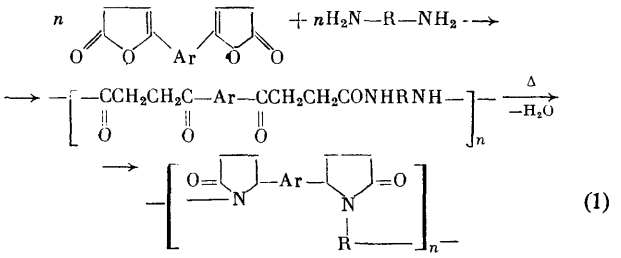
1. *bis*-γ-Lactones

Unsaturated γ-lactones are much less reactive than β-lactones. However, they are more reactive than the corresponding linear analogues, alkyl esters of carboxylic acids, which are exceptionally unreactive toward aminolysis.[39–43] Reaction of a *bis*-γ-lactone with aliphatic diamines (65–80 °C, 20 days, in alcohols and diethyleneglycol) produces hydrophilic polyamides containing hydroxyl groups with $\eta_{inh} \leqslant 0.53$ dl g^{-1}.[44,45]

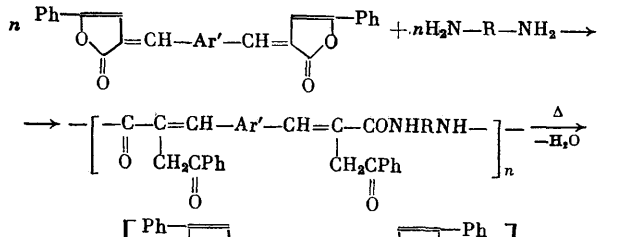


Unsaturated *bis*-γ-lactones are more reactive toward aminolysis. They react with aliphatic diamines to produce polyamides with $\eta_{inh} \leqslant 0.8$ dl g^{-1}.[45,47] In this instance the effect of ring strain is apparently not "innocent" since the unsaturated lactones are cyclic

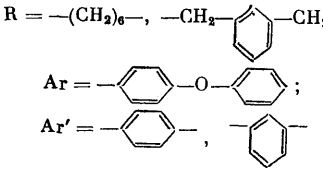
analogues of vinyl esters, which are more reactive toward aminolysis than their saturated analogues.[39] This is due to the greater electronegativity of a vinyl group compared with an alkyl group. An additional driving force for starting with an unsaturated alcohol is the ease of isomerisation into a stable ketone. Here we note that whereas the reaction of diamines with unsaturated *bis*-lactones forms polyamides containing hydroxyl groups, reaction with unsaturated *bis*-lactones produces polyketoamides containing keto groups in the main [Reaction (1)][47] or side [Reaction (2)] chain:[46]



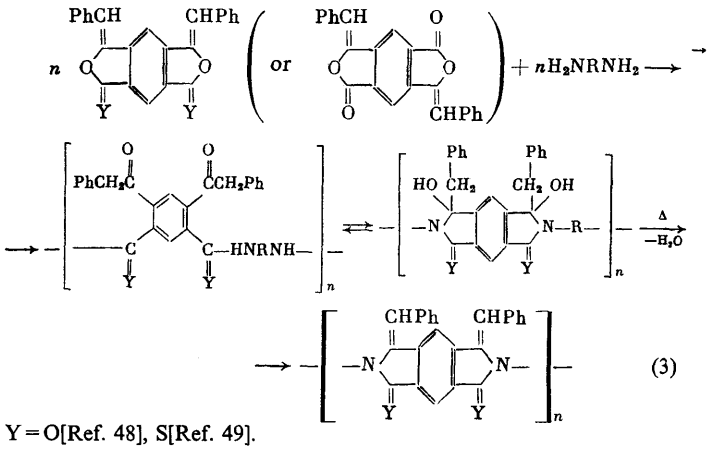
(1)



(2)



The *bis*-benzylidene derivatives of pyromellitic[48] and pyromellitdithioic[49] anhydrides (pyromellitides) react analogously with diamines:



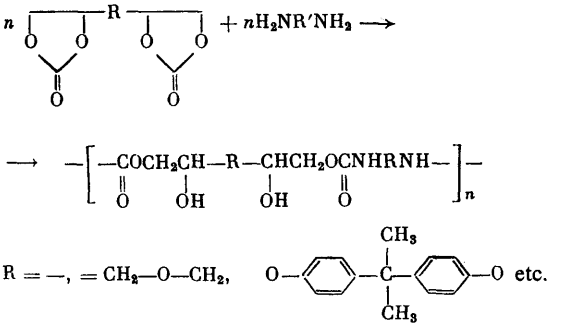
(3)

Y = O[Ref. 48], S[Ref. 49].

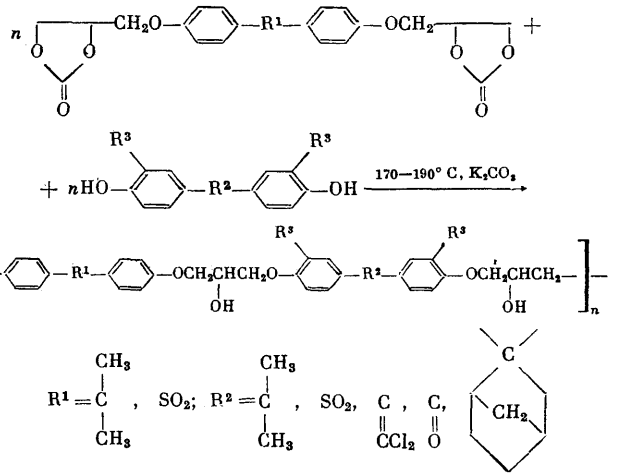
Other 3,5- and 3,7-disubstituted pyromellitides (for example, see Ref. 49 and references cited above) have also been synthesised. It has been demonstrated that benzylidene-substituted pyromellitides are more reactive toward diamines than phenyl-substituted ones and that those containing S are more reactive than the analogues containing O. Polyimidines with good heat resistance and solubility in organic solvents are obtained by cyclodehydration of the intermediate polyketoamides [or the cyclic hydroxy forms, see Reaction (3)]. It is noteworthy that the polyketoamides mentioned above [see Reactions (1) and (2)] also undergo cyclodehydration to the corresponding polymeric heterocyclic compounds.

2. Cyclic *bis*-carbonates

Cyclic *bis*-carbonates also readily react by ring opening and polycondensation with aliphatic diamines. Thus, hydrophilic polyurethanes ([η] ⩽ 1.0 dl g^{-1}) containing hydroxyl groups are formed:[50–53]



It was found[54] that cyclic *bis*-carbonates in the melt or in a polar aprotic solvent (DMSO, sulpholane) at 170–190 °C in the presence of K_2CO_3 alkylate *bis*-phenols, forming simple polyethers‡ containing hydroxyl groups ([η] = 0.3–0.7 dl g^{-1}):



R^3 = H, CH_3.

The synthesis of polymers through reaction of anhydrides of unsaturated dicarboxylic acids (maleic, itaconic, cyclohexen-1,2-dicarboxylic, etc.) with cyclic carbonates (ethylene- and

‡ Polymers of this class are also obtained through reaction of *bis*-phenols with diepoxides or epichlorohydrin (cf. Part II).

propylenecarbonate) has been reported. Depending on the reaction conditions, either crosslinked or linear polymers with $\eta_{inh} \leqslant 0.21$ dl g^{-1} are formed.[55] This reaction apparently can be extended to cyclic *bis*-carbonates.

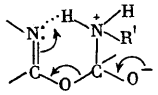
Syntheses involving cyclic *bis*-carbonates are rather attractive since, on one hand, monomers are obtained through reaction of diepoxides (of independent interest as starting monomers, cf. Part II) with CO_2 and, on the other, polymers, in particular, polyurethanes, are obtained by a scheme avoiding use of highly toxic phosgene.

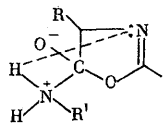
3. *bis*-Azlactones

a) Saturated *bis*-azlactones

Some of the first representatives of cyclic bifunctional monomers of this class were saturated azlactones, 2,2′-*p*-phenylene (or polymethylene)-*bis*-(oxazoline-5-one). These were first synthesised by cyclisation of *N,N′*-diacyl-*bis*-α-aminoacids§ and used to synthesise polymers by Cleaver and Pratt in 1955.[56,57]

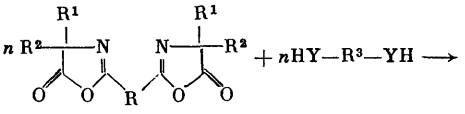
It is noteworthy that azlactones contain the isoimide structural moiety $-N=C-O-CO-$, which is distinguished by a great propensity to react with nucleophiles.[58–60] Adducts of carbodiimides and carboxylic acids containing analogous structural elements also are exceptionally reactive toward nucleophiles.[61,62] This feature along with the ring strain apparently is responsible for the high acylating potential of azlactones. However, it must be mentioned that aminolysis in linear isoimides can be accelerated owing to the freedom of intramolecular rotation taking into account anchimeric assistance from the isoimide N atom in the transition complex. This should be hindered in the cyclic analogues (azlactones) although the existence of a similar effect in the latter instance also cannot be completely ruled out:



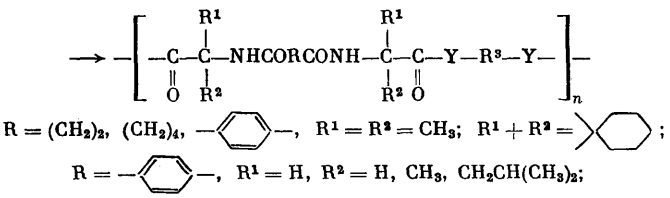


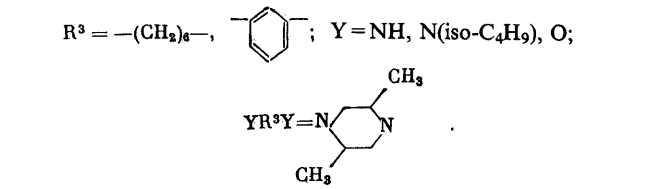
A study of the kinetics of anilinolysis of 4,4′-R-substituted 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) demonstrated[63] that they are comparable in reactivity to *p*-nitrophenyl esters of aliphatic carboxylic acids.[64,65] Thus, it was also demonstrated that 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) are monomers with an independent reactivity of functional groups and that the radical R in the 4-position of the azlactone ring has comparatively little effect on their reactivity.

Cleaver and Pratt[57] used various 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) to synthesise regularly alternating polymers, mainly polyamides, containing α-aminoacid moieties in the principal macromolecular chains:



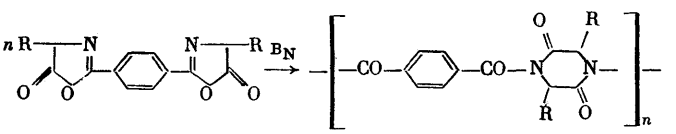
§ Obtained through reaction of the dichloroanhydrides of dicarboxylic acids with α-aminoacids.[56]





High-molecular-weight polyamides were prepared based on aliphatic diamines. An aromatic diamine and aliphatic diol were used to synthesise low-molecular-weight polymers.

It was found[57] that 2,2′-*p*-phenylene-*bis*-oxazolinones in the presence of a tertiary amine (B_N) undergo homopolymerisation to form poly(*N,N′*-terephthaloyl-diketopiperazine):



These compounds are polymeric acyllactams (activated amides) and are very reactive toward nucleophiles.[6] In analogy with polyanhydrides,[66] they can be used as quickly decomposing materials for medical and biological applications.

Other investigators[67–70] subsequently also prepared various 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) and used them to synthesise ordinary polyamides. A slightly different path to *N,N′*-diacyl-*bis*-α-aminoacids, reaction of dinitriles with an α-hydroxyacid (benzylic) according to Ritter, has been proposed.[68]

The variety of α-aminoacids used to synthesise 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) has been significantly expanded.[71] As a result, polyamides and copolyamides that contain enzyme-specific side groups in the macromolecules and are susceptible to biodegradation have been prepared.[72] These polyamides exhibit good biocompatibility and are promising as surgical materials.[73,74] The rapid rate of reaction of 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) with aliphatic diamines[71] determined the ability to prepare block-copolymers based on telechelic oligopeptides containing terminal amino groups. Such block-copolymers undergo biodestruction at an incresed rate[72,75] and are promising as drug delivery systems.

Table 1. Saturated five-membered *bis*-azlactones used to synthesise polymers.

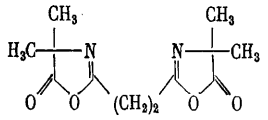
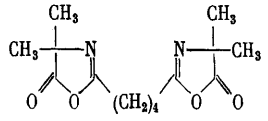
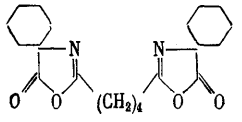
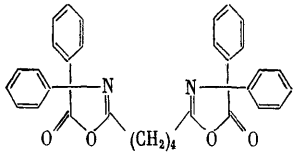
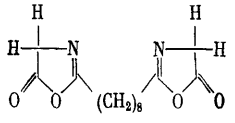
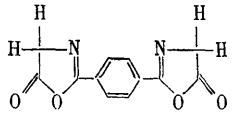
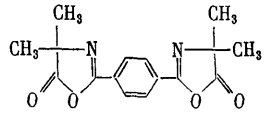
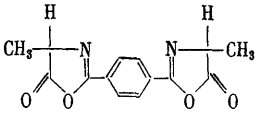
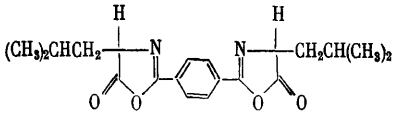
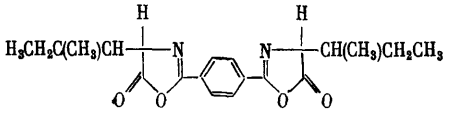
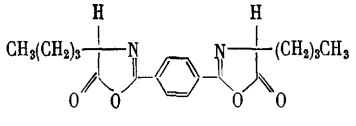
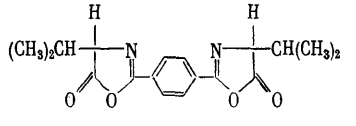
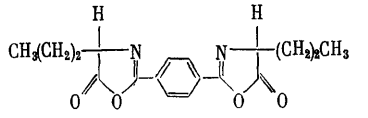
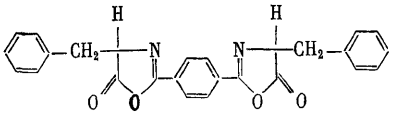
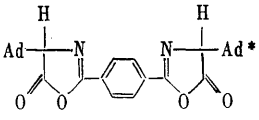
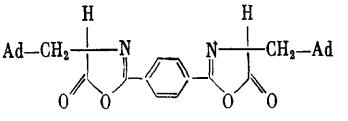
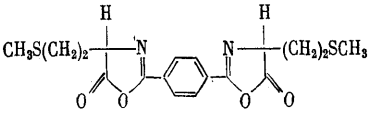
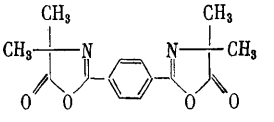
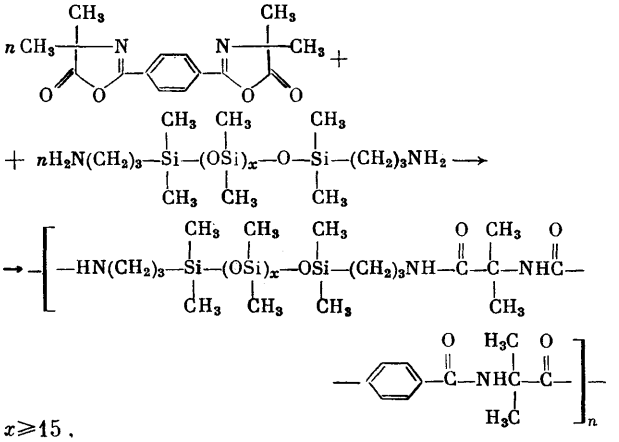
bis-Azlactone	Reference
	[56]
	[56, 57]
	[56, 57]
	[68—70]
	[67]
	[56, 57, 71, 78, 79]
	[56, 57, 78, 79]
	[46, 47, 71, 75]
	[56, 57, 67, 71, 75]
	[71, 75]
	[71, 75]
	[71, 75]

Table 1. (contd.)

bis-Azlactone	Reference
	[71, 75]
	[71, 75]
	[75]
	[75]
	[71, 75]
	[78, 79]

*Ad = adamantyl

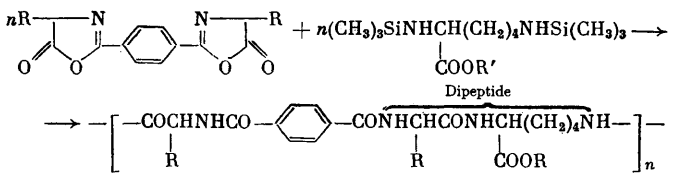
An alternating block-copolymer was also prepared on the basis of telechelic oligosiloxanes:[76]



$x \geqslant 15$.

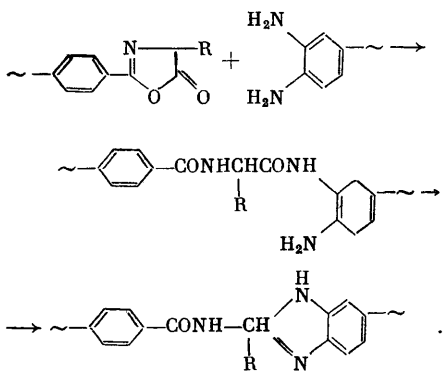
It has been demonstrated that *bis*-(oxazoline-5-ones) react with *N,N'*-trimethylsilylated diamines to form high-molecular-weight polyamides ($[\eta] \leqslant 0.68$ dl g^{-1}).[75]

This reaction was successfully used to prepare polyamides with dipeptide fragments using alkyl esters of N^{α},N^{β}-*bis*-trimethylsilyl-L-lysine as the diamine:[75,77]



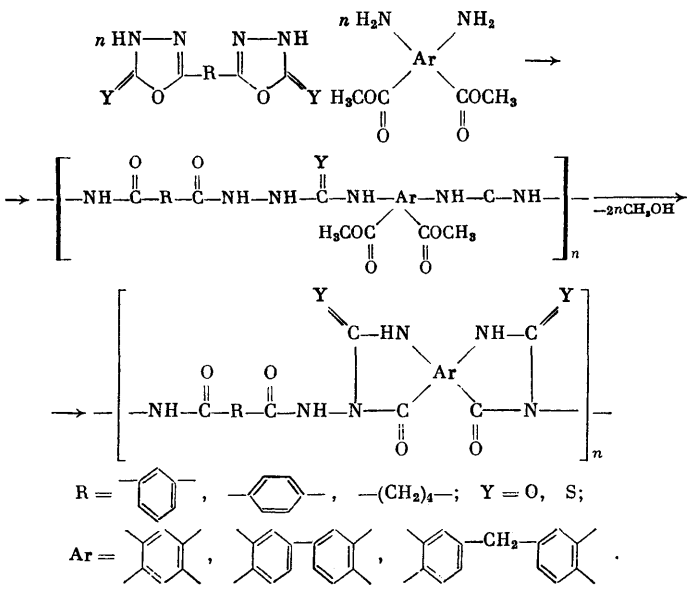
$R' = CH_3$, C_2H_5.

Polyamidobenzimidazoles have been prepared through reaction of 2,2′-*p*-phenylene-*bis*-(oxazoline-5-ones) with tetraamines:[78,79]



The saturated five-membered *bis*-azlactones used to synthesise polymers are presented in Table 1.

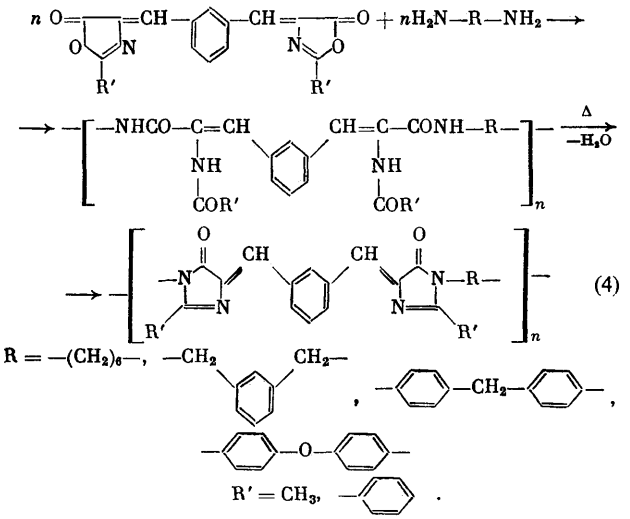
Iwakura, et al.[80,81] used five-membered azlactones with two N atoms in the ring, 2,2′-arylene (or alkylene)-*bis*-(1,3,4-oxadiazoline-5-ones) and 2,2′-arylene (or alkylene)-*bis*-(1,3,4-oxadiazoline-5-ones), as bifunctional cyclic monomers in polycondensation with *bis*-*o*-aminoesters:



The reaction was carried out in *m*-cresol at 180 °C (Y = O;[80] [η] of the obtained polyamidequinazolinediones is 0.09–0.27 dl g^{-1}) or at 150–160 °C (Y = S;[81] [η] of the obtained polyamidequinazoline-4-one-2-thiones is 0.07–0.31 dl g^{-1}). The comparatively mild reaction conditions in the latter instance may be related to the greater reactivity of the analogue containing S.

b) Unsaturated azlactones

Ueda, et al., who have greatly contributed to the development of the active-ring method, synthesised unsaturated *bis*-azlactones[82] and investigated their polycondensation with diamines:

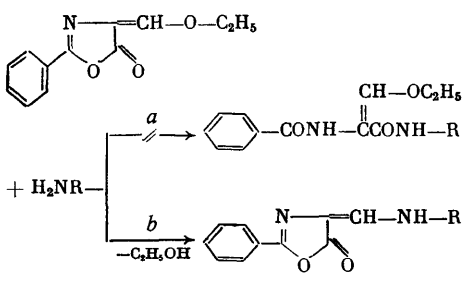


(4)

It was found that unsaturated *bis*-azlactones are sufficiently reactive to synthesise polymers (η_{inh} = 0.17–0.51 dl g^{-1}). However, as should have been expected,[83] they are inferior to the saturated analogues. In all probability the reason for the poorer reactivity of the unsaturated azlactones should be sought both in the conjugation of the heterocyclic carboxylic group with the C–C double bond, which decreases its electrophilicity, and in the ring conjugation of the electrons that stabilises the azlactone ring in general.

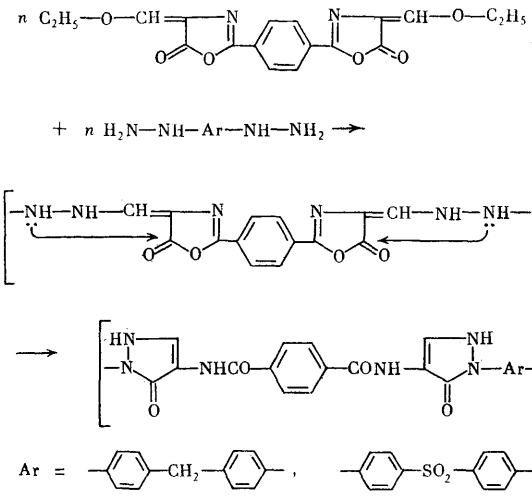
It was suggested that the unsaturated polyamide that was formed with pendant amide groups undergoes cyclodehydration with formation of the corresponding polyimidazolone [Reaction (4)] near 200 °C for R = $(CH_2)_6$ and R′ = CH_3.

It is interesting that the ring is stabilised so much if the 2,2′-*p*-phenylene-*bis*-azlactone contains an ethoxymethylene group as the substituent in the 4,4′-positions that it is not opened by amines. Instead of acylation [Reaction (5*a*)], nucleophilic substitution occurs [Reaction (5*b*)]:

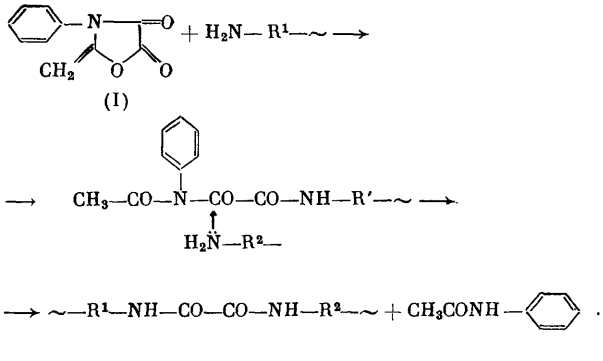


(5)

This fact was established by Imai, et al.,[84–87] who prepared high-molecular-weight polyenamines containing azlactone rings in the principal chains of the macromolecules instead of the expected polyamides through reaction of the corresponding *bis*-azlactone with diamines. The polycondensation of a *bis*-azlactone with aromatic dihydrazines occurs analogously in the first step. However, in this instance the reaction proceeds further with involvement of a second N atom of the hydrazine and is accompanied by opening of the azlactone ring and intramolecular rearrangement.[86] As a result, high-molecular-weight (η_{inh} = 0.5–1.23 dl g^{-1}) polyamide-pyrazolines are formed:



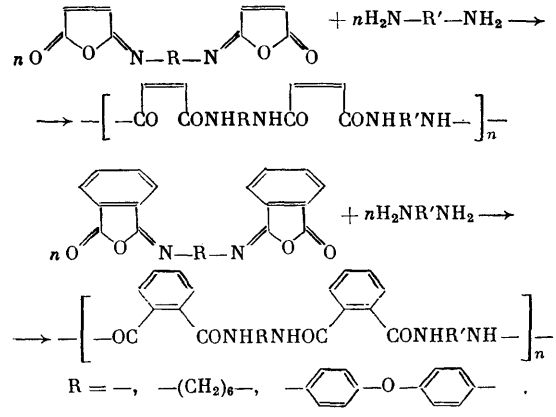
An original method of synthesising polyoxamides is based on use of an unsaturated monoazlactone, 2-methylene-3-phenyloxazolidine-4,5-dione (I), exhibiting Φ_{pr} = 2. The ring opens in the first step of the reaction of this compound with diamines. In the second, aminolysis occurs with loss of acetanilide and the polyoxamide forms ($\eta_{inh} \leqslant$ 0.35 dl g^{-1}):[88]



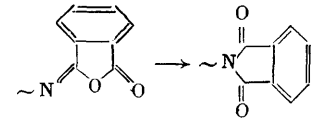
This process is a unique combination of two methods of activated polycondensation. These are the active-ring method and the leaving-group (active-amide) method.[6]

4. Cyclic *bis*-isoimides and *bis*-imides

The synthesis of various *bis*-isoimides has been reported.[89–91] These are structural isomers of the *bis*-azlactones examined above. As was expected, the isoimides react readily with aliphatic diamines in aprotic polar solvents at room temperature to give the corresponding polyamides:

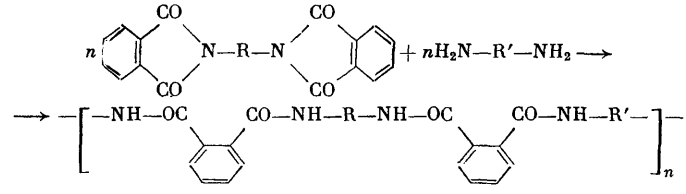


The *bis*-maleic isoimides were more reactive. Reaction of these with *m*-xylylenediamine in *N*-methylpyrrolidone is complete after 1 h.[89] They react with aromatic 4,4′-diaminodiphenyloxide much more slowly. The reaction is complete only after three days. Polyamides based on *bis*-maleic isoimides had higher viscosities ($\eta_{inh} \leqslant$ 0.7 dl g^{-1}) than those based on *bis*-isophthalimides ($\eta_{inh} \leqslant$ 0.26 dl g^{-1}). This and the slow rate of the principal reaction are related to the ease of isomerisation of the latter to the corresponding phthalimides. This inhibits chain propagation:[90]



For this reason the use of high temperature to accelerate the reaction of *bis*-isophthalimides with diamines is undesirable.

However, it was demonstrated that under certain conditions (in dry organic solvents, e.g. toluene at 20–95 °C) the ring opens during reaction of polymethylene-*bis*-phthalimides with aliphatic diamines. This leads to polyphthalimides ([η] $\leqslant$ 0.32 dl g^{-1}):[92,93]



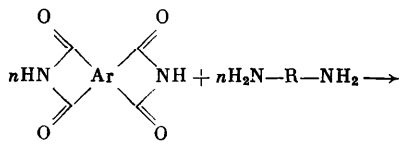
(6)

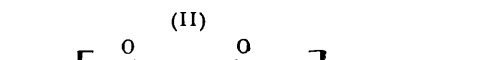
where R = $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_6-$, and $-(CH_2)_{10}-$.

It is noteworthy that Reaction (6) does not occur in the presence of water. Furthermore, other *bis*-imides (see above) react better with diamines in aqueous medium.

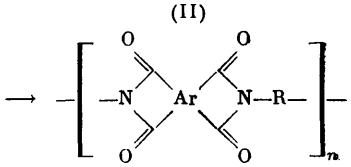
For example, Zhubanov, et al.,[94,95] synthesised the polyamido-amides (II) through reaction of imides of aromatic tetracarboxylic acids with aliphatic diamines in aqueous suspension at room

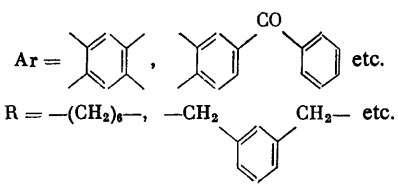
temperature. Alkylaromatic polyimides were prepared by cyclisation of these at 200–250 °C:



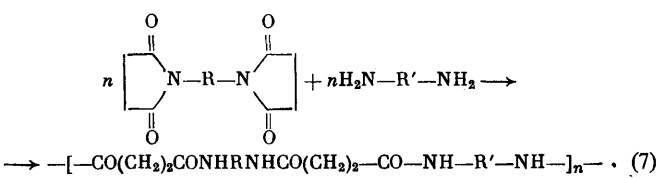


(II)





In contrast with aromatic phthalimides (the imide ring is stabilised by conjugation with the benzene ring), the ring of aliphatic imides, in particular, *N,N'*-alkylene-*bis*-succinimides, tends to open during reaction with aliphatic diamines. This forms the corresponding polysuccinamides:

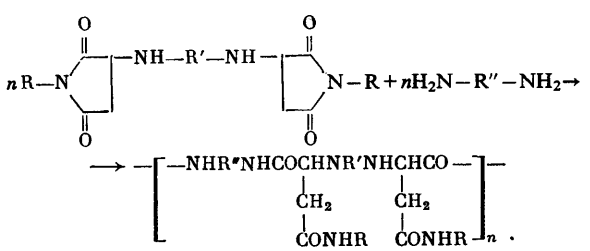


(7)

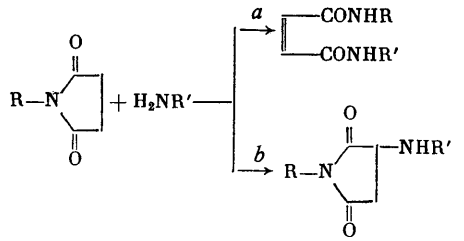
Kagiya, et al.[96] carried out this reaction in the melt at 200 °C and produced polyamides with $[\eta] = 0.2-0.5$ dl g^{-1}.

It has been found[97] that this reaction occurs better (under mild conditions of 0–20 °C) in aqueous ethanol to produce polysuccinamides with a relative molecular mass up to 20×10^3. It is interesting that Reaction (7), in contrast with Reaction (6), practically does not occur in dry and in polar aprotic solvents.

Diimides of *bis*-aspartic acid have also been used as starting monomers in reactions analogous to Reaction (7):[98]

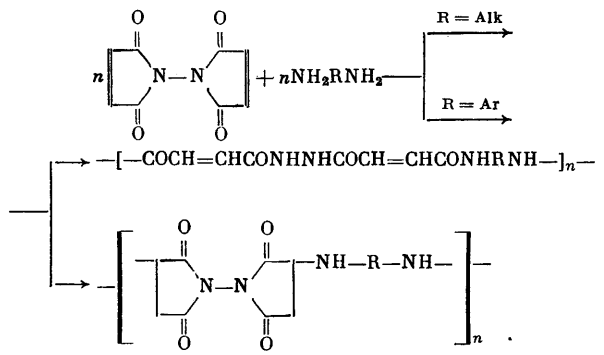


Cycloimides based on unsaturated acids, e.g. maleic and citraconic,[99] are also capable of being opened by amines. This reaction also occurs in aqueous medium [Reaction (8*a*)]. The amine adds to the double bond in anhydrous organic solvents [Reaction (8*b*)]:[100]



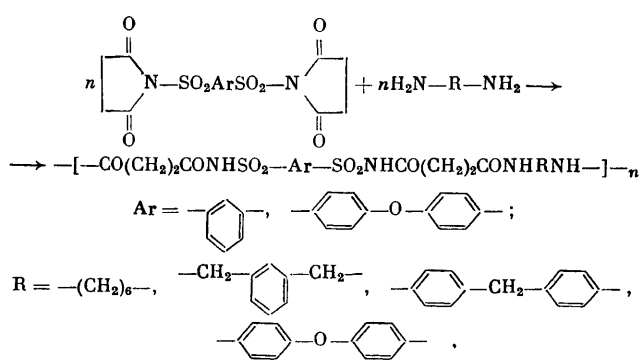
(8)

The direction of the reaction depends on the nature of the amine.[100] For example, *N,N'-bis*-maleimide in *m*-cresol at 65 °C with aliphatic diamines forms polyamides ($\eta_{inh} \leqslant 0.98$ dl g^{-1}) whereas addition to the double bond occurs for aromatic diamines to form polysuccinimides ($\eta_{inh} \leqslant 0.56$ dl g^{-1}):

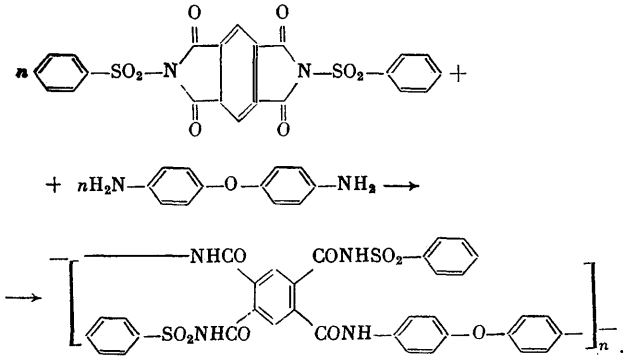


It is noteworthy that polyamides based on 1,2-dicarboxylic acids are promising as self-destructive polymers since the neighbouring amide groups facilitate hydrolytic decomposition of each other.[101]

Activated imides containing electron acceptor groups on the N atom were more reactive toward amines. For example, it was found that *N,N'*-arylenedisulphonyl-*bis*-succinimides react with diamines in *N*-methylpyrrolidone at 10–20 °C to form polyamides with $\eta_{inh} \leqslant 0.4$ dl g^{-1}.[102]

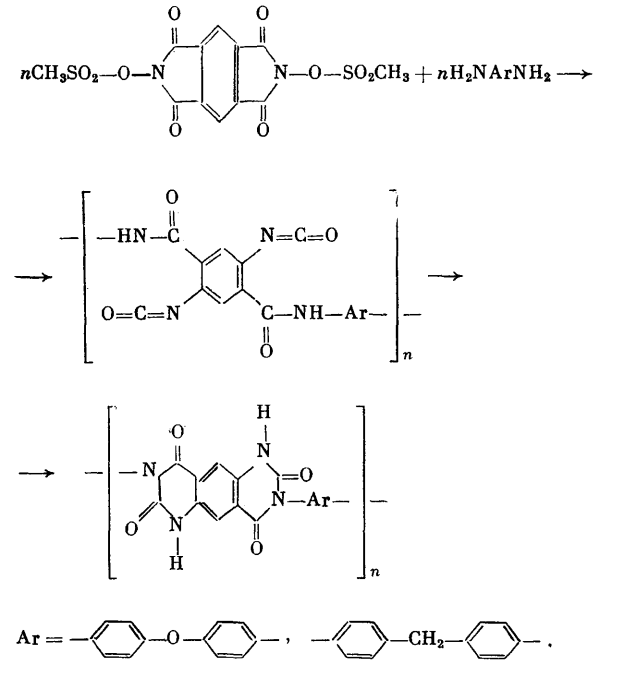


The reaction of *N,N'-bis*-(phenylsulphonyl)pyromellitimide with an aromatic diamine (η_{inh} of the polyamide formed = 0.74 dl g^{-1}) occurs analogously at room temperature:[103]

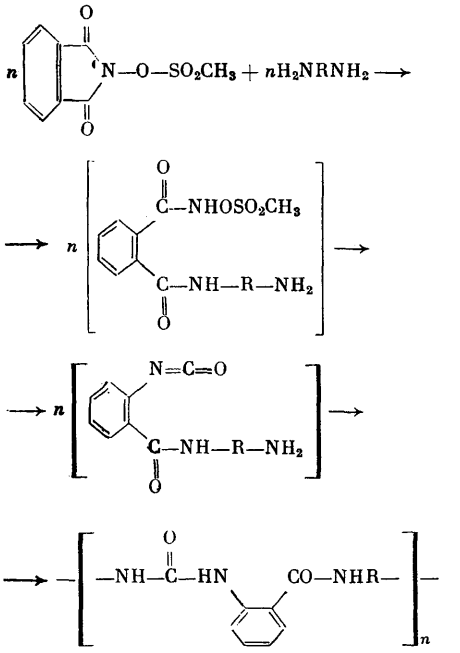


It is noteworthy that the reaction of *N*-arylsulphonylimides and diamines occurs with ring opening and without cleavage of the $=N-SO_2-$ bond whereas the exocyclic $=N-CO-$ bond primarily cleaves during aminolysis of *N*-acylimides with loss of the corresponding imide.[6]

The mesyloxy group also substantially activates the imide ring. In this instance the mesylhydroxamic acid formed undergoes the Lossen rearrangement. Polyquinazolinediones ($\eta_{inh} \leqslant 0.25$ dl g^{-1}) are formed as a result:[104]

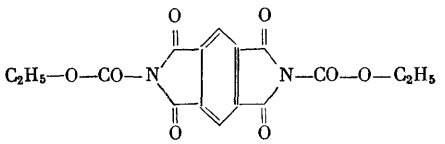


Thanks to the rearrangement mentioned above the *N*-mesylphthalimide exhibits $\Phi_{pr} = 2$ with diamines (at a 1 : 1 mole ratio). This leads to formation of polybenzamidoureas:[105]



The synthesised polymers have low viscosities (η_{inh} = 0.12–0.34 dl g^{-1}). Apparently this is due to chain breaking as a result of cyclisation of the intermediate isocyanate to the corresponding quinazolinedione.

An ethoxycarbonyl group also activates the phthalimide ring towards reaction with amines.[106] For example, *N,N'-bis*-(ethoxycarbonyl)pyromellitimide



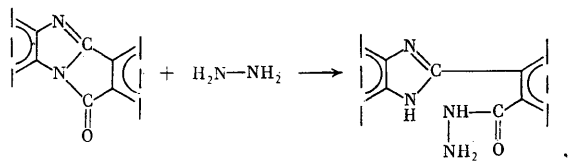
is significantly more reactive than the unsubstituted pyromellitimide; however, it is less so than the *N,N'-bis*-phenylsulphonyl derivative examined above. The latter in turn is less active than pyromellitic dianhydride. The *N*-substituted pyromellitimides, like pyromellitic dithioanhydride, were polymerised[107] during a search for better methods of synthesising pyromellitimides. An important advantage of these compounds is the ease of cyclisation of the prepolymers prepared from them compared with the polyamido acid synthesised through pyromellitic dianhydride.

The polymerisation involving cycloimides (both with opening and without opening of the imide ring) are discussed in more detail in a review.[12]

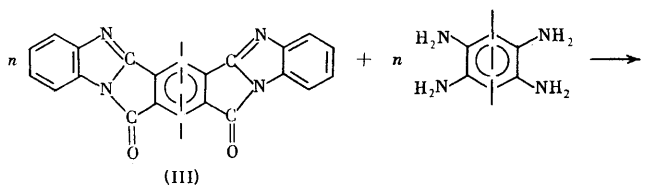
5. Cyclic *bis*-amides

Korshak, et al.[108] found in 1969 that benzoylenebenzimidazoles (benzimidazopyrrolones) are intramolecularly activated amides (their acyclic analogues have since been widely used to synthesise

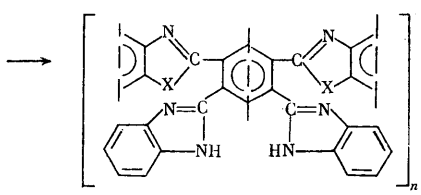
polyamides[6]) and readily react with a highly basic nucleophile (hydrazine) under mild conditions:



Then *bis*-benzoylenebenzimidazoles (III, IV) were successfully used as monomers both for the synthesis of various polybenzazoles with *o*-benzimidazole substituents in the principal chains of the macromolecules:[109–111]

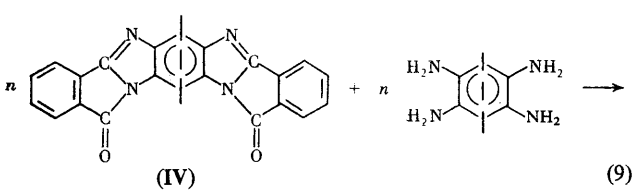


(III)

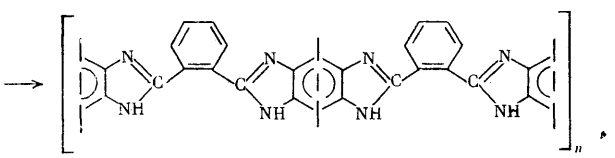


X = O, S, NH.

and for the synthesis of copolymers of polybenzimidazoles[112] with a regular alternation of two tetraamine residues.

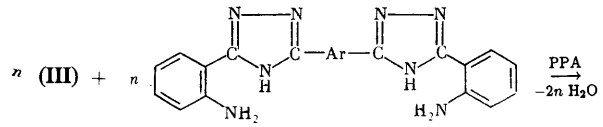


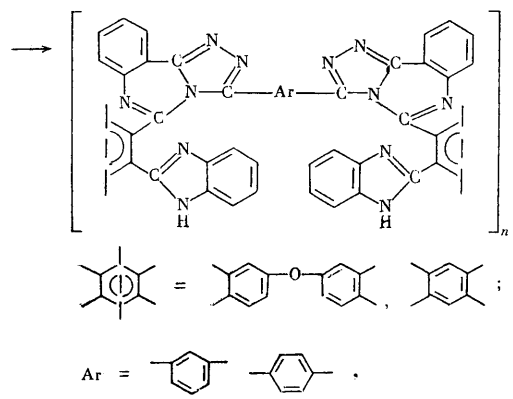
(IV) (9)



These reactions were carried out in polyphosphoric acid (PPA) at 180–200 °C. The prepared polymers are soluble in organic solvents and are capable of forming layers.

In analogous reactions in PPA, *bis*-[5-(*o*-aminophenyl)-*s*-triazolyl-3]phenylenes were used with III as tetrafunctional nucleophiles.[113] This resulted in block-ladder soluble polytriazoloquinazolines with *o*-benzimidazole side groups:





In contrast with the five-membered benzoyleneimidazoles, six-membered naphthoylenebenzimidazoles containing the structural element

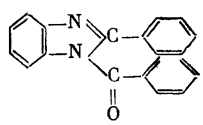
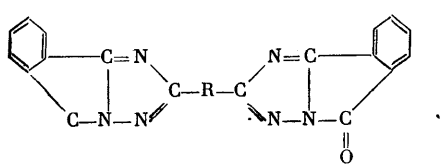
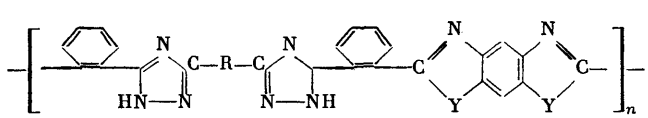


exhibit high chemical resistance[114] and do not undergo analogous reactions.

It has been demonstrated[115] that *bis*-benzoylenetriazoles of the general formula below can be used as bifunctional cyclic activated amines to synthesise polyheteroarylene through Reaction (9):

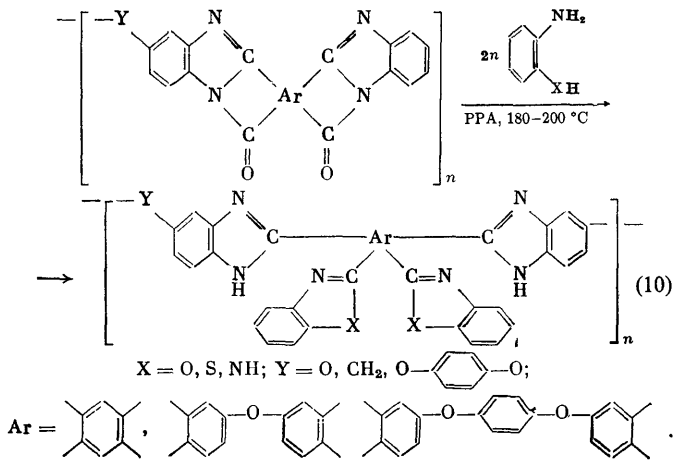


Copolymers with a regular alternation of benzazole and triazole rings in the principal chains of the macromolecules are produced:



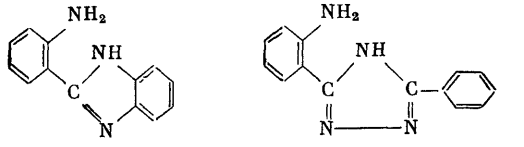
Y = O, S, NH.

Reactions similar to those given above have also been used for polymer-like conversions of polybenzoylenebenzimidazoles in order to prepare modified polybenzimidazoles:[116]



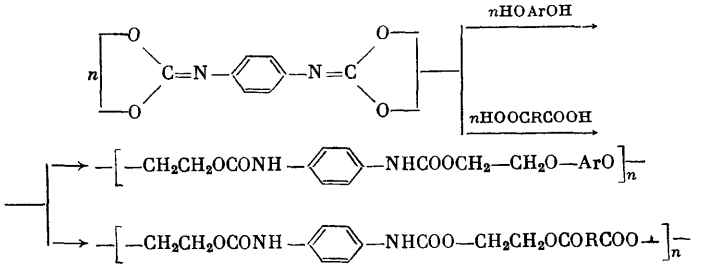
(10)

In order to increase the heat resistance and solubility of the polymers, 2-(*o*-aminophenyl)-benzimidazoles and 3-phenyl-5-(*o*-aminophenyl)-1,2,4-triazoles have been employed as the *o*-substituted anilines in Reaction (10):[117]

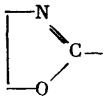


6. Cyclic *bis*-iminoesters and their analogues

An interesting method of synthesising polyesterurethanes consisting of the reaction of a bifunctional cyclic iminocarbonate with *bis*-phenols[118] and dicarboxylic acids[119] has been proposed by Mukayama, et al.

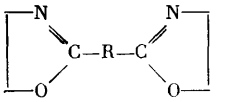


Bifunctional oxazolines containing the structural element



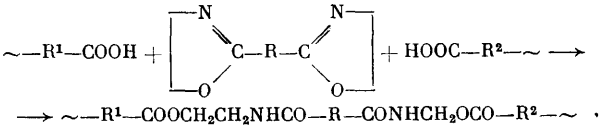
were used to synthesise hetero-chain polymers by various authors. These can be viewed as cyclic iminoesters.

bis-Oxazolines of general formula



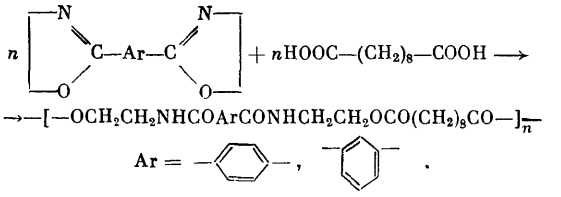
R = —[Ref. 120], —C6H4—[Ref. 121];

have been used[120,121] as chain extenders of polyesters with terminal carboxylic groups:

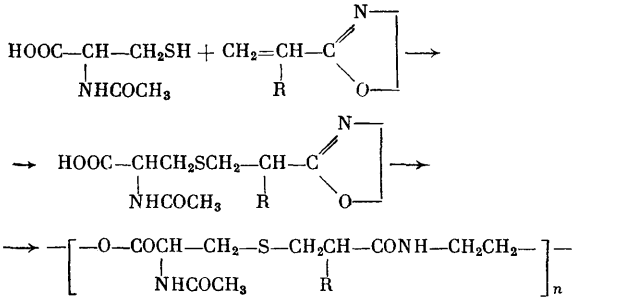


It is noteworthy that the reaction was carried out at elevated temperatures (200—280 °C) in the polyester melt. Under these conditions the stable *bis*-oxazolines are more suitable chain extenders than their more thermally resistant analogues, the *bis*-oxazolinones examined in part 4.

The reaction of oxazolines with carboxylic acids was investigated in detail and used successfully by Sano[122] to synthesise high-molecular-weight polyesteramides ($[\eta] \lesssim 1.21$ dl g^{-1}) in the mass at 185—240 °C:

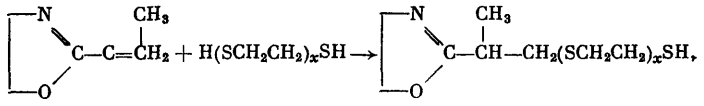


An original synthesis route to polyesteramides employing unsaturated 2-alkylene-2-oxazoline has been proposed.[123] An AB-type monomer is first prepared by its reaction with *N*-acetyl-L-cysteine:

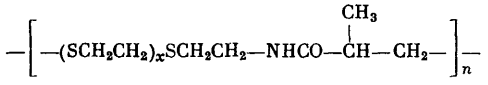


where R = H and CH_3. This is then polymerised with the terminal carboxylic and oxazoline group (analogously to the reactions mentioned above). The mechanism involves polyaddition in DMF at 50—100 °C and produces an optically active polymer with a relative molecular mass up to 13.8×10^3.

An essentially similar process has been carried out.[124] Reaction of 2-isopropenyl-2-oxazolines with H_2S or a dithiol was used to synthesise AB-monomers with SH- and oxazoline groups:

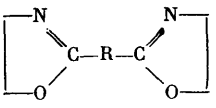


where $x = 0$ and 1. The latter was polymerised in the melt or DMF at 100–200 °C. Polyamidethioethers were prepared with the structure:



with $M_n \leqslant 4300$ depending on the reaction conditions.

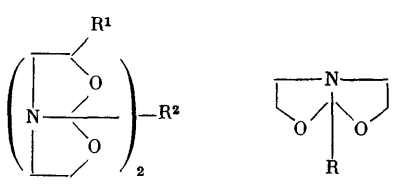
The nucleophilic substitution reaction on which the processes described above are based was also used to prepare polyamides containing simple ether bonds through reaction of *bis*-oxazolines of general formula



where R = alkylene C_{1-20} and arylene C_{6-20}, with polyphenols at 170 °C using $Ph_3(C^+X^-$ (X = BF_4, PF_6, SbF_6, AsF_6, BPh_4, or ClO_4) as catalysts.[125] High-melting thermally reactive polyamidoethers with a 5% mass loss at 390 °C (TGA) were obtained.

The *bis*-oxazolines also react with aromatic diamines to form prepolymers that undergo intermolecular crosslinking in the presence of strong acids as catalysts.[126] These systems are useful for preparing thermally reactive formed compositions with good strength indicators.

Bicyclic amidacetals of the general formula shown below with structures similar to the iminoethers were also used as cyclic monomers to prepare polymers:



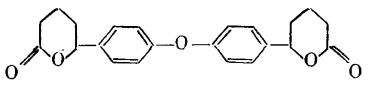
Reaction of these with alkanolamines produces oligomeric polyols that are used to synthesise polyurethanes.[127]

Polyurethanes are also synthesised through reaction of bicyclic amidacetals with polyols and diisocyanates[128] or directly with diisocyanates.[129]

V. Six-membered heterocycles

1. *bis*-δ-Lactones

Six-membered *bis*-δ-lactones are unreactive in aminolysis reactions, like their five-membered analogues (see Part IV). The *bis*-δ-valerolactone shown below has been synthesised:[130]



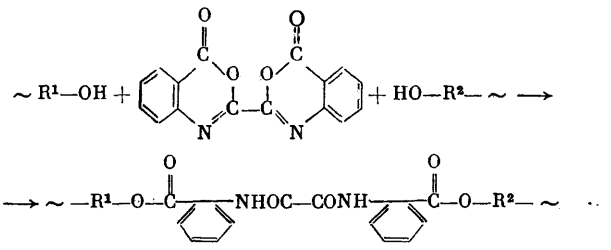
It was found that a polyamide containing hydroxyl groups with $\eta_{inh} \leqslant 0.26$ dl g^{-1} is formed through its reaction with hexamethylenediamine (65–80 °C, 10 days, in methanol, *m*-cresol or *N*-methylpyrrolidone).

2. *bis*-Benzoxazinones

Ueda and Imai[131] synthesised various *bis*-(3,1-benzoxazine-4-ones) (Table 2, compounds Nos. 1–6) from *bis*-anthranilic acids. These are six-membered analogues of isoimide azlactones (Part IV). During a study of model reactions it was established that these compounds at room temperature comparatively easily react with aliphatic amines (butylamine, benzylamine). More forcing conditions are required with an aromatic amine (aniline). This is probably due to both the decrease of electrophilic reactivity of the isoimide fragment (its carbonyl group) and the significant stabilisation of the heterocycle owing to conjugation with the condensed benzene ring. It was found that 2-methyl-substituted benzoxazines are more active than the 2-phenyl-substituted analogues. This may also indicate the importance of conjugation in determining the acylating potential of a given heterocyclic system.

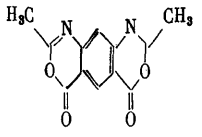
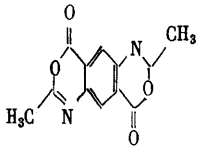
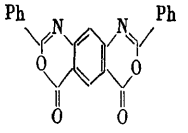
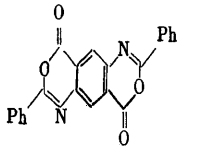
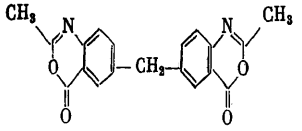
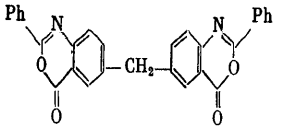
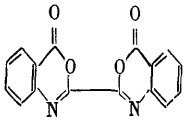
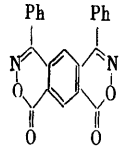
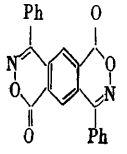
High-molecular-weight layer-forming polyamides with $\eta_{inh} \leqslant 0.6$ dl g^{-1} are produced through reaction of *bis*-benzoxazinones with hexamethylenediamine and *m*-xylylenediamine in polar aprotic solvents (DMF, hexametapol, DMSO, etc.).[131]

Inata and Matsumura[132] also synthesised the novel isoimide benzoxazinone 2,2′-*bis*-(4H-3,1-benzoxazine-4-one) and used it as a chain extender of polyethyleneterephthalate:



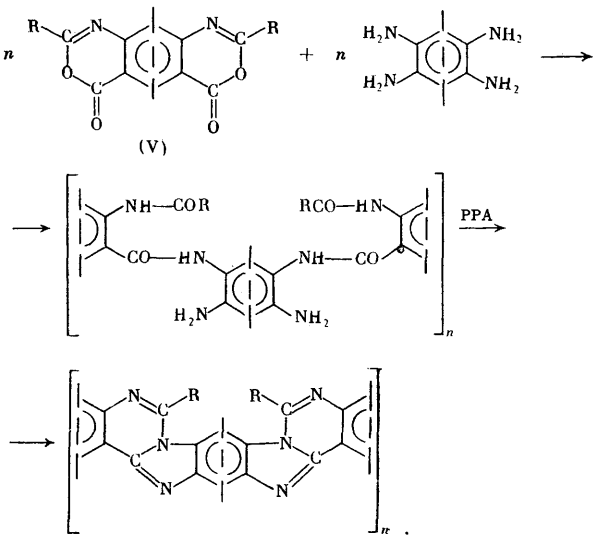
The reaction was carried out in the melt at 280 °C. A linear polymer with an elevated molecular mass was prepared. It is appropriate to mention here that *bis*-oxazinones, as was expected, react with OH groups with more difficulty than five-membered azlactones.

Table 2. *bis*-Oxazinones used to synthesise polyamides.

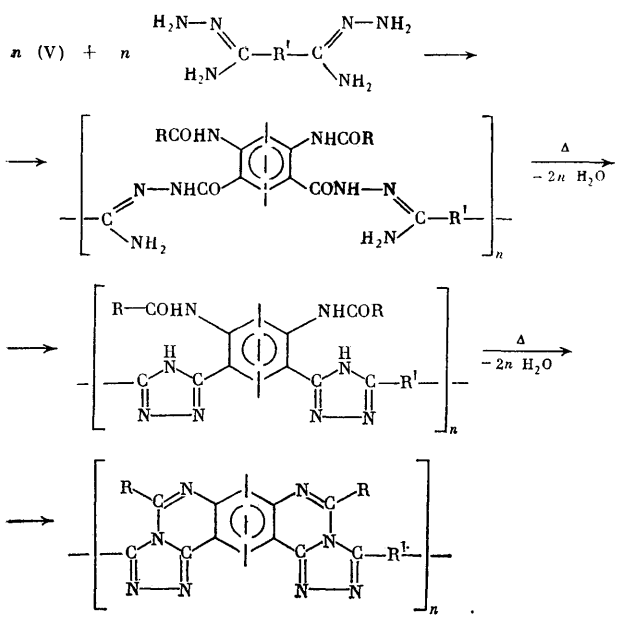
Sample No.	*bis*-Oxazinone	Reference
1		[131]
2		[131]
3		[131]
4		[131]
5		[131, 133]
6		[131]
7		[132]
8		[137]
9		[137]

Quinazoloneimide¶[133] copolymers with an initial decomposition temperature of 380–396 °C are obtained through reaction of 6,6′-methylene-*bis*-(2-methyl-3,1-benzoxazine-4-one) (Table 2, compound No. 5) with 4,4′-diaminodiphenyloxide and 3,3′,4,4′-benzophenonetetracarboxylic acid in *m*-cresol in the temperature range 130–180 °C.

The reaction of isoimide *bis*-benzoxazinones with *bis*-*o*-phenylenediamines (aromatic tetraamines) was used to synthesise full or partial ladder polymers, polybenzimidazolequinazolines:[134,135]



Korshak, et al.[136] used *bis*-amidrazones as tetrafunctional nucleophiles in the reaction with *bis*-benzoxazinones to synthesise partial ladder (block–ladder) polytriazoloquinazolines:

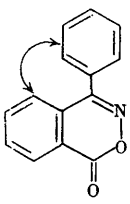


The isomeric *bis*-oxazinones *bis*-4-phenyl-2,3-benzoxazine-1-ones (Table 2, compounds Nos. 8 and 9) were also synthesised.[137] In contrast with the benzoxazinones examined above that contain isoimide moieties, the reactive structural elements of the

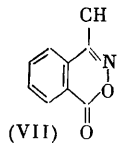
¶ Adducts of *bis*-benzoxazione and diamines undergo thermal cyclodehydration to form polyquinazolones.

benzoxazinones that are isomeric with them are O-acyloxime fragments $-CO-O-N=C\diagup\diagdown$, which are distinguished by a comparatively low acylating potential.[138,139]

A study of model reactions demonstrated that the 4-phenyl-substituted 1H-2,3-benzoxazine-1-one (VI) readily reacts with aliphatic amines (*n*-butylamine and benzylamine) at 20 °C to form the corresponding adducts in quantitative yields regardless of the solvent nature (ethanol, THF, *N*-methylpyrrolidone). This azlactone does not react with aniline even under more forcing conditions (at 80 °C). In contrast with VI, its 4-methyl-substituted analogue (VII) is stable and does not react even with aliphatic amines at 80 °C.

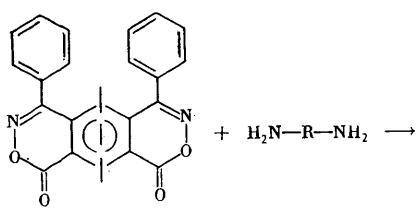


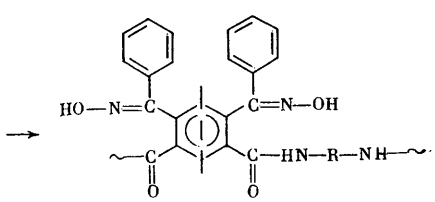
(VI)



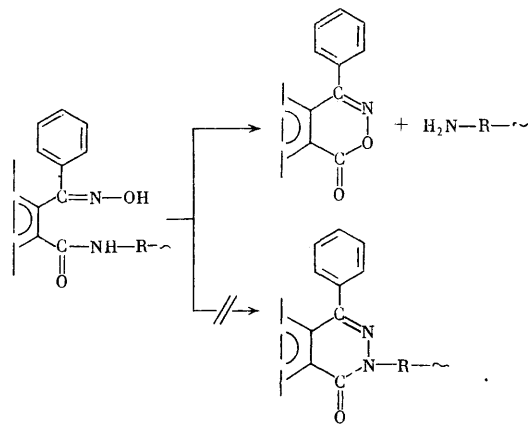
(VII)

Therefore, acyloxime benzoxazinones are much less reactive than the isoimide analogues. The higher reactivity of VI compared with its linear analogues[138,139] may be due to both strain in the ring and steric interaction between the benzene rings (shown by an arrow), which is relieved after opening of the heterocycle by aminolysis. Polycondensation of 4-phenyl-substituted benzoxazinones (Table 2, compounds Nos. 8 and 9) with aliphatic diamines in aprotic polar solvents at 20 °C is complete after 2–3 days. Polyamides are formed in quantitative yields. However, they have comparatively low viscosities (η_{inh} = 0.12–0.38 dl g^{-1}).





This and the low reactivity of the heterocycle may be due to the equilibrium nature of the reaction. This view is consistent with the ease of depolymerising the polyamide at elevated temperature (220 °C):



- - -o0o- - -

The polymer syntheses examined in the present review are stepwise polyaddition processes that obey the rules of polycondensation. A number of the reactions, for example, those involving saturated *bis*-azlactones, *bis*-isoimides and *bis*-imides, in addition to certain unsaturated *bis*-azlactones, are polyaddition processes in the pure sense. In the remaining instances, some groups or others (hydroxyls, ketones, etc.) are lost that formally can be viewed as low-molecular-weight side products. However, these do not abandon the macromolecular chains and remain bonded to them by a covalent bond. Such reactions are promising for the synthesis of various functionalised polymers including those for biomedical applications.

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