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Copolymerisation of Cyclic Compounds

T.M.Frunze and V.V.Kurashev

The number of studies dealing with the synthesis of copolymers and the investigation of the copolymerisation of cyclic monomers of a single class is large. The present review is concerned with the polymerisation of cyclic compounds, in which the ring is opened, with monomers of other classes, i.e. of a different chemical type. These processes include the copolymerisation of a number of cyclic compounds with olefins and also the copolymerisation of two cyclic compounds of different classes. The conditions of synthesis, the mechanism of formation, and certain properties of such copolymers are considered. The bibliography comprises 88 references.

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I. INTRODUCTION

The study of copolymerisation is of great practical and theoretical importance. Copolymerisation permits the desired modification of the properties of polymers. Sometimes the properties of copolymers differ appreciably from those of the corresponding homopolymers, while in other cases the copolymers combine the properties characteristic of the homopolymers.

The copolymerisation of vinyl monomers has been investigated comparatively thoroughly. Many reviews and monographs describing both the theoretical aspects of the process and the problems of the practical application of various copolymers have been published. The polymerisation and copolymerisation of cyclic compounds has been studied much less adequately. However, the number of papers published in this field increases from year to year.

The polymerisation of cyclic compounds has assumed increasing importance as a general method of synthesis of high-molecular compounds. The principal advances in this field were achieved in the industrial polymerisation of lactams, epoxy-compounds, and certain other cyclic monomers.

In the copolymerisation of cyclic compounds the following principal cases can be distinguished: (1) copolymerisation of cyclic compounds of the same chemical type (for example different lactones or epoxy-compounds); (2) copolymerisation of cyclic compounds with vinyl compounds; (3) copolymerisation of cyclic compounds of different chemical types (for example lactones with epoxy-compounds, etc.). From the theoretical standpoint, the first case is not of fundamental interest, since, in view of the identical chemical type of the monomers, the polymerisation mechanism does not differ from the mechanism of homopolymerisation and the process is determined merely by the kinetic and thermodynamic factors associated with the structure of the monomers. In contrast, the last two cases are extremely interesting from both the theoretical and practical points of view. They give rise to new opportunities for the synthesis of high-molecular compounds both as regards the development of new methods and the synthesis of new copolymers, and they extend the range of monomers suitable for copolymerisation.

The study of the copolymerisation of cyclic compounds has not been as detailed as that of vinyl monomers and the copolymerisation of cyclic compounds with compounds of other chemical types has been studied to an even lesser extent. There is no doubt, however, that such copolymerisation is of great interest and an attempt is made in the present review to give a systematic account of the available literature data on this question.

Polymerisation with ring opening is frequently called polyaddition. It takes place in stages (for example, hydrolytic polymerisation) or is a chain reaction (for example, ionic polymerisation). In the polymerisation of cyclic compounds the products are hetero-chain polymers, which can be obtained also by the polycondensation of certain bifunctional compounds. However, a characteristic feature of the polymerisation of cyclic compounds is that the compositions of the monomer and polymer are the same, i.e. in polymerisation with ring opening chemical bonds of types other than those in the monomer are not produced, the bonds being merely redistributed. Thus the initial monomer and the polymer formed in the polymerisation of cyclic compounds belong to the same chemical class.

Polymerisation has a number of advantages over polycondensation. Thus, in order to obtain polymers with high molecular weight by polycondensation, the proportions of the starting components must be rigorously equimolar and provision must be made for sufficiently effective removal from the reaction sphere of the low-molecular products evolved. In the polymerisation of cyclic compounds this is not necessary and the polymers formed have as a rule a high molecular weight.

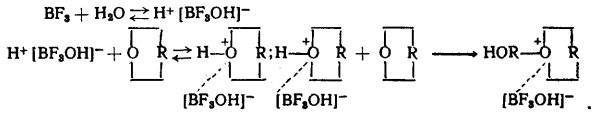
II. COPOLYMERISATION OF CYCLIC COMPOUNDS WITH OLEFINS

The copolymerisation of cyclic compounds with olefins has been investigated relatively little. It usually takes place via an ionic, usually cationic, mechanism, although there are indications that this type of polymerisation occurs also in the presence of radical initiators. Examples of this kind of polymerisation are quoted in Table 1.

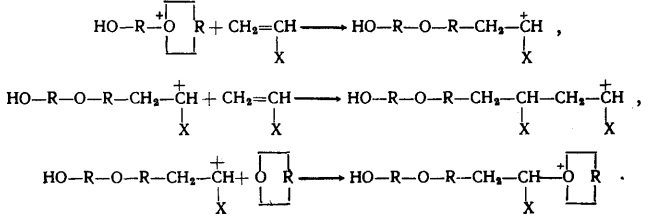
1. Ionic Copolymerisation

a. Cationic copolymerisation. The copolymerisation of cyclic compounds with olefins takes place mainly by a cationic mechanism, which may be because of the particular range of co-monomers investigated at the present time. These are mainly cyclic ethers, lactones, and certain other oxygen-containing compounds.

The initiation of the polymerisation of cyclic ethers in the presence of Lewis acids can be represented as follows:



When this mechanism is extended to the copolymerisation of cyclic ethers with olefins, the formation of copolymers can be represented thus:

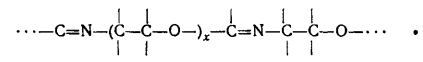


The possibility of the cationic copolymerisation of cyclic ethers and olefins was demonstrated by Merten[1], who achieved the copolymerisation of the following combinations of monomers in the presence of boron trifluoride-ether: styrene–olefin (propene, styrene) oxide, styrene–epichlorohydrin, chloroprene–olefin (propene, styrene) oxide, propene oxide–olefin (isobutene, propene, divinylbenzene), and epichlorohydrin–acrylonitrile. The copolymerisation yielded liquid copolymers. Liquid polyesters with terminal hydroxy-groups are formed in the cationic copolymerisation of epichlorohydrin with styrene in the presence of linear polyacetals and boron trifluoride-ether[2]. In contrast to the previous investigations, Minoura and Minton[3] obtained solid copolymers of epichlorohydrin and styrene by carrying out the reaction in benzene solution in the presence of boron trifluoride-ether. In the first stages of the reaction the copolymer is enriched in epichlorohydrin units. The authors suggest that the first reaction step is the interaction of epichlorohydrin with the catalyst. Gurgiolo[4] described a method for the preparation of solid copolymers

of epoxyalkanes with a number of unsaturated monomers, the copolymers having relatively high softening points (120–190°C) and readily forming very flexible films. The copolymerisation of epoxy-compounds (epichlorohydrin, epoxyethane, epoxypropane) with unsaturated compounds (vinylidene chloride, methyl methacrylate, butadiene) was carried out in the presence of the complex of ferric chloride and the epoxy-compound.

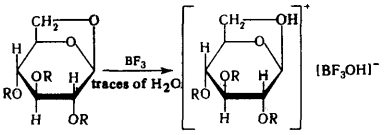
Durgaryan and Beginyan[5] described the copolymerisation of epichlorohydrin with aceto- and benzo-nitriles carried out in the solid phase at 70°C in the presence of 5 mole % $SnCl_4$ as catalyst. It is interesting that, under the conditions chosen, the nitriles taken separately do not polymerise. The formation of copolymers was demonstrated by fractional precipitation. In addition it was shown that the dependence of the composition of the copolymers on that of the initial mixture follows the equation characterising the composition of a copolymer. The copolymerisation constants are $r_1 = 4.2 \pm 0.4$ and $r_2 = 0 \pm 0.02$ for epichlorohydrin and acetonitrile and $r_1 = 2.8 \pm 0.2$ and $r_2 = 0 \pm 0.02$ for epichlorohydrin and benzonitrile.

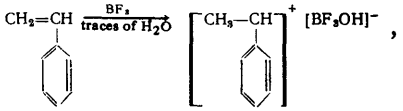
Since in the hydrolysis of copolymers the acids corresponding to the nitrile are formed quantitatively, together with compounds containing amino-groups, it was concluded that the copolymerisation of nitriles with epichlorohydrin does not involve the formation of new carbon–carbon bonds. The following structure was assigned to the copolymer:



Parnikis et al.[6] investigated the copolymerisation of trimethyl-laevoglucosan with styrene under the influence of boron trifluoride-ether. The formation of a copolymer was demonstrated by fractional precipitation, turbidimetric titration, and by thermomechanical compression curves. The following mechanism is proposed for the formation of copolymers.

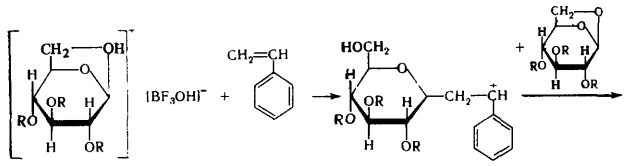
(a) Initiation:

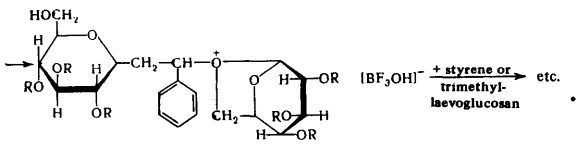




or

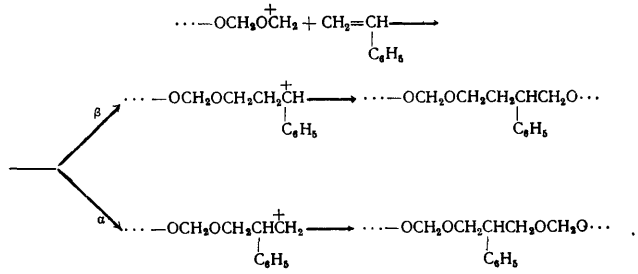
(b) chain growth:



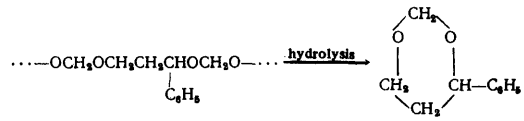


Parnikis et al.[6] believe that, in view of the different reactivities of the oxonium and carbonium ions, initially styrene polymerises preferentially and then trimethyl-laevoglucosan. When styrene or methylmethacrylate is allowed to act on the "live" tetramethyl-laevoglucosan polymer obtained under the influence of boron trifluoride, the corresponding block-copolymers are produced.

Trioxan (a cyclic ether) can also enter into cationic copolymerisation with styrene, vinyl ethers, and acrylonitrile[7]. It is suggested that the copolymerisation of trioxan with styrene takes place under the action of free carbonium cations. The polymeric chain can grow by the addition of a carbonium ion derived from trioxan to the α- or β-carbon atom of the vinyl group in styrene[8]:



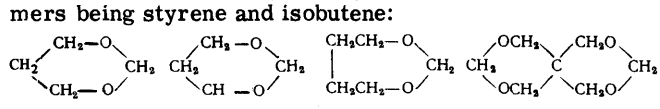
4-Phenyl-1,3-dioxan was isolated after the acid hydrolysis of the copolymer[9]:



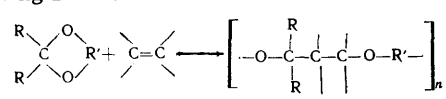
This is evidence of the addition of the carbonium ion to the β-carbon atom of styrene.

There are indications in the literature that the copolymers obtained in the cationic copolymerisation of trioxan with vinyl monomers are thermostable products capable of being worked by pressing (at 190°C and a pressure of 105 atm)[10]. Such copolymers can be used for the manufacture of flexible strips and films[11]. In order to copolymerise dioxan with vinyl monomers, catalysts other than boron triofluoride–ether can be used, for example triethyl or trimethyl hexachloroantimonate, bis(triethyloxonium) hexachlorostannate, trimethyl-, triethyl-, or tri-n-propyloxonium fluoroborate, etc.[11]

Cyclic formals have been polymerised with vinyl compounds[12]. The copolymers thus obtained are low-molecular liquid products with terminal hydroxyls. They are recommended for use in the synthesis of polyurethane rubbers. The cyclic formals used were 1,3-dioxan (A), 4-phenyl-1,3-dioxan (B), tetramethyleneformal (C), and the diformal derived from pentaerythritol (D), the vinyl monomers being styrene and isobutene:

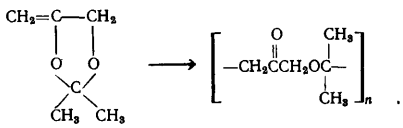


Sulphuric acid or polystyrenesulphonic acid and glycols such as butane-1,4-diol or 1,4-di-(β-hydroxyethoxy)butane were used as catalytic systems. It is suggested that copolymerisation leads to the formation of a copolymer having the following structure:



Okada and coworkers[13] investigated the cationic copolymerisation of 1,3-dioxolan with styrene in toluene solution at 25°C in the presence of boron trifluoride-ether. On the basis of the results obtained after the extraction of the product with hot water and methanol, it is suggested that a true copolymer is formed. The apparent constants for the copolymerisation of 1,3-dioxolan with styrene calculated from the Mayo–Lewis equation are respectively $r_1 = 1.9$ and $r_2 = 0.35$. It has been shown by NMR and by hydrolysing the copolymer that the 1,3-dioxolan ring opens during the reaction at the O_1-C_2 bond.

An interesting example of the formation of polymers involving the opening of the ring and of the multiple bond is the homopolymerisation of 2,2-dimethyl-4-methylene-1,3-dioxolan. Goodman and Abe[14] showed that, in the presence of boron trifluoride-ether, the polymerisation of 2,2-dimethyl-4-methylene-1,3-dioxolan takes place both with participation of the vinyl group and via ring opening and is accompanied by intramolecular rearrangement:



Lactones constitute another type of cyclic compounds capable of undergoing cationic copolymerisation with olefins. The copolymerisation takes place in the presence of stannic chloride or boron trifluoride-ether[15,16]. It has been found that cross propagation takes place with difficulty and under the conditions investigated appreciable amounts of block copolymers are formed. The authors explained this result by the formation in the reaction sphere of a specific complex of the lactone and the catalyst ($SnCl_4$) which catalyses the polymerisation of the lactone but not that of styrene. The authors note that the polymerisation of styrene and its copolymerisation with the β-lactone depend on the content of free catalyst (for example $SnCl_4$) in the reaction mixture, which is determined by the polarity of the solvent in which the copolymerisation is carried out.

In a polar solvent (for example in nitrobenzene) the amount of free stannic chloride increases. The content of lactone units in the copolymer is then reduced.

Although the nature of the complex of the lactone and the catalyst is unknown, the results obtained and also comparison with its catalytic capacity in homopolymerisation (for example of phthalide) show that the formation of the catalyst–cyclic monomer complex is an important factor controlling the copolymerisation of vinyl and cyclic compounds.

b. Anionic Copolymerisation. The anionic copolymerisation of vinyl monomers with cyclic compounds is carried out in the presence of initiators which form either free or co-ordinately bound anions. Under these conditions copolymerisation is rare—usually the homopolymerisation of both the cyclic and the vinyl monomer takes place.

Table 1 lists the known examples of anionic copolymerisation of cyclic compounds, mainly epoxy-compounds, with olefins. Thus Tsuruta and Fujio[17] showed that, in the presence of catalysts such as aluminium alkoxides, methyl vinyl ketone copolymerises with certain epoxy-compounds (epoxypropane or epichlorohydrin). The copolymerisation was carried out in benzene solution at 80°C for three days. The formation of a real copolymer is indicated by the agreement between the results of its investigation by turbidimetric titration and by infrared spectroscopy. Since the infrared spectrum of the copolymer does not contain absorption bands characteristic of the double bond and there are bands corresponding to the carbonyl group, it is suggested that the copolymerisation involves the opening of the ring of the epoxy-compound and of the double bond of the olefin.

Okamura and Hayashi[18] described the copolymerisation of olefins (ethylene, propene) oxides with acrylonitrile under the influence of γ-radiation. Successful copolymerisation depends to a considerable degree on the reaction temperature: at room temperature only the homopolymer of acrylonitrile is formed, while at low temperatures (between −178 and −196°C) copolymers are produced. As the reaction temperature is reduced, the content of olefin oxide units in the copolymer increases. The fact that epoxypropane does not polymerise by a radical mechanism and also the occurrence of the reaction at low temperatures suggest an anionic reaction mechanism in this case, but special studies designed to elucidate the mechanism of copolymerisation were not undertaken.

Lactones are also capable of polymerising with certain unsaturated compounds under the influence of anionic catalysts. Shimosaka et al.[19] carried out the copolymerisation of β-propiolactone with acrylonitrile at room temperature in the presence of various anionic catalysts: $SrZn(C_2H_5)_4$, $Al(C_2H_5)_3$, naphthalenesodium, $C_4H_9Li + Al(C_2H_5)_3$, and $B(C_4H_9)_3 + Cd(C_2H_5)_2$. Copolymerisation results in the formation of polymeric products which can be separated into fractions soluble and insoluble in chloroform. The chloroform-soluble fraction is the homopolymer of β-propiolactone, while the insoluble fraction consists of the homopolymer of acrylonitrile and its copolymer with β-propiolactone.

Shiota et al.[20] achieved the grafting of β-propiolactone onto polyacrylonitrile. Potassium hydroxide, sodium methoxide, and butyl-lithium were used as catalysts of the graft copolymerisation of the β-lactone with polyacrylonitrile.

Apart from the copolymerisation reactions of cyclic compounds with olefins examined above, examples of block-copolymerisation are known. Thus Richards and Szwarc[21] and also Finaz et al.[22] obtained block-copolymers of styrene with epoxyethane. The reaction of "live" polystyrene with epoxyethane results in the formation of terminal ... $CH_2CH_2\bar{O}\dot{N}a$ group, capable of adding epoxyethane with formation of copolymers in which the polystyrene block is included between polyepoxyethane blocks. Such copolymerisation goes almost to completion. When the same reaction is carried out with epoxypropane, only 25% of the epoxy-compound copolymerises. Probably in this case chain transfer to epoxypropane takes place and leads to the formation of a polyepoxypropane homopolymer. Furukawa et al.[23] obtained a block-copolymer of acrylonitrile with epoxyethane, using the alkoxide of polyepoxyethane as the catalyst.

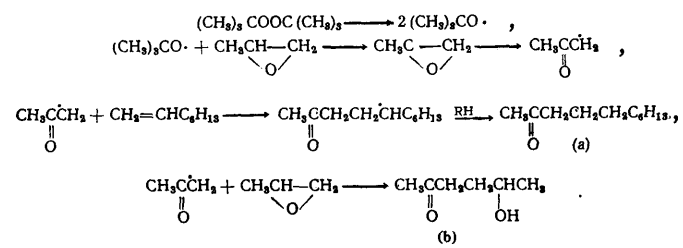
2. Radical Copolymerisation

The radical copolymerisation of olefins with cyclic compounds has been least investigated. Indeed, while the addition of free radicals to atoms attached to a double bond has been known for a long time[24], the process has been inadequately elucidated for various cyclic compounds. In general radicals show a greater tendency to combine with hydrogen or any other reactive atom or group than to effect ring opening. Probably this is why radical copolymerisation of olefins with cyclic compounds is difficult.

Nevertheless cases are known where carbon and other rings open under the influence of free radicals. This has been demonstrated in reactions of low-molecular organic

compounds. For example, in the free-radical chlorination of spiropentanes chloro-derivatives of aliphatic hydrocarbons are formed[25].

Gritter[26] achieved the addition of epoxypropane to oct-1-ene in the presence of t-butyl peroxide; 2-undecanone (a) and 5-hydroxy-2-hexanone (b) were isolated in low yields. By carrying out the reaction at a lower temperature (below 125°C), it proved possible to obtain only the second compound. The authors suggest the following reaction mechanism:



Radicals formed from epoxypropane isomerise to keto-radicals, which are capable of reacting both with the double bond and with the epoxy-ring. Further development of the reaction is difficult due to termination which occurs when the radicals react with hydrogen atoms. The last of the stages enumerated above prevents the formation of a polymeric chain. However, despite the absence of communications on the homopolymerisation of olefin oxides under the action of radical initiators, the possibility of ring opening by a radical mechanism cannot be excluded[25,27]. Nor can one exclude the possibility of the copolymerisation of olefins with cyclic compounds, the occurrence of which has been confirmed in a number of studies quoted below. Examples of the radical copolymerisation of certain cyclic compounds, mainly epoxy-compounds, with olefins are presented in Table 1.

Table 1. Copolymers of cyclic compounds and olefins.

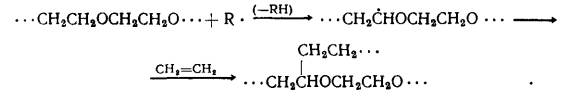
Co-monomers	Type of catalyst: radical	anionic	cationic	Refs.
Epoxyethane-				
-ethylene	benzalazine	–	–	28
-vinylidene chloride	potassium persulphate	–	$FeCl_3$.epoxypropane	30, 4
-chlorotrifluoroethylene	t-butyl peroxide	–	–	34
-perfluoropropene	ditto	–	–	34
-butadiene	–	–	$FeCl_3$.epoxypropane	4
-styrene	–	–	naphthalenesodium	21
	–	–	phenylisopropyl-potassium or methylstyrene tetramer	22
Epoxypropane-				
-vinylidene chloride	potassium persulphate	–	$FeCl_3$.epoxypropane	30, 4
-propene	–	–	BF_3-ether	1
-isobutene	–	–	ditto	1
-butadiene	–	–	$FeCl_3$.epoxypropane	4
-chloroprene	–	–	BF_3-ether	1
-methyl methacrylate	–	–	$FeCl_3$.epoxypropane	4
-methyl vinyl ketone	–	tri-isopropyl-aluminium	–	17
-styrene	–	naphthalene-sodium	BF_3-ether	1, 2, 23
-divinylbenzene	–	–	ditto	1
Epichlorohydrin-				
-vinylidene chloride	–	–	$FeCl_3$.epoxypropane	4
-butadiene	–	diethylzinc + nickel or cadmium di-halide-di(tri-alkyl)phos-phite	ditto	4, 38
-methyl methacrylate	–	–	"	4
-styrene	–	–	BF_3-ether	1, 2, 3
-acrylonitrile	–	–	ditto	1
-acetonitrile	–	–	stannic chloride	5
-benzonitrile	–	–	ditto	5
-methyl vinyl ketone	–	tri-isopropyl-aluminium	–	17
Chloroprene oxide-				
-vinylidene chloride	–	–	$FeCl_3$.epoxypropane	4
-butadiene	–	–	ditto	4
-methyl methacrylate	–	–	"	4
Butadiene oxide-				
-vinylidene chloride	potassium persulphate	–	–	30
Styrene oxide-				
-butadiene	cumenyl hydro-peroxide sodium sulphate	–	–	31
-chloroprene	–	–	BF_3-ether	1
-styrene	–	–	ditto	1

Table 1. (cont'd).

Co-monomers	Type of catalyst: radical	anionic	cationic	Refs.
Trioxan-				
-acrylonitrile	–	–	*p*-nitrophenyl-diazonium fluoroborate	11
-styrene	–	–	BF_3-ether	7, 8
-vinyl acetate	–	–	ditto	7
-isobutyl vinyl ether	–	–	"	10
-methyl vinyl ketone	–	–	"	7
1,3-Dioxolan-				
-isobutene	–	–	sulphuric acid or polystyrenesul-phonic acid	12
-styrene	–	–	BF_3-ether	12, 13, 39
4-Phenyl-1,3-Dioxolan-				
-isobutene	–	–	sulphuric acid or polystyrenesul-phonic acid	12
-styrene	–	–	ditto	12
4-Chloromethyl-1,3--dioxolan				
-styrene	–	–	BF_3-ether	39
Tetramethyleneformal-				
-isobutene	–	–	sulphuric acid or polystyrenesulphonic acid	12
-styrene	–	–	ditto	12
Diformal of pentaerythritol-				
-isobutene	–	–	"	12
-styrene	–	–	"	12
Trimethyl-laevoglucosan-				
-styrene	–	–	"	6
β-Propiolactone-				
-ethylene	di-t-butyl peroxide	–	–	32
-styrene	–	–	stannic chloride, BF_3-ether	15, 16
-acrylonitrile	–	naphthalene-sodium, tri-ethylalumi-nium, butyl-lithium-tri-ethylalumi-nium, tributyl-boron-diethyl-cadmium	–	19, 40
-polyacrylonitrile	–	butyl-lithium, potassium hy-droxide, sodium methoxide	–	20

The radical copolymerisation of 1,2-epoxy-compounds with olefins takes place mainly at high temperatures. Coffman[28] described the copolymerisation of ethylene with epoxyethane, which was carried out at 200–250°C under a pressure of 350–1000 atm in the presence of benzalazine as the initiator. The copolymers obtained contained between 5 and 15 mole % of epoxyethane. When the copolymer was treated with hydrobromic acid, most of the epoxyethane units were eliminated in the form of ethyl bromide. This shows that most of these units are arranged consecutively in the copolymer and that the latter is an antistatic agent. Furthermore polyepoxyethane, which can form by a non-radical mechanism, as a result of the presence of ether

links in the main chain, can readily give up hydrogen atoms to radicals. Consequently there is a possibility of the formation of graft copolymers via a chain-transfer reaction:



In 1949 a method for the copolymerisation of dec-1-ene with epoxyethane was patented[29]. The reaction was carried out at 260–370°C for 10 h.

Stanton and Lowry[30] obtained a series of copolymers of vinylidene chloride with the oxides of ethylene, propene, and butadiene. The copolymerisation was carried out in aqueous emulsion using potassium persulphate as the initiator. In contrast to the unmodified poly(vinylidene chloride), the copolymers with epoxyethane had lower softening temperatures (about 135°C) and contained polyepoxyethane, which could not be extracted with water. However, this is not sufficient evidence for postulating the formation of a non-ordered copolymer.

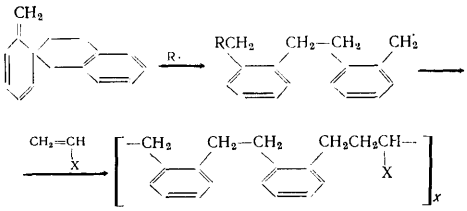
Ponomarev et al.[31] described a study on the copolymerisation of styrene oxide with butadiene in the presence of cumenyl hydroperoxide. It was shown that the polymerisation of styrene oxide and butadiene in aqueous emulsion at 5°C leads to the formation of a copolymer with a high molecular weight.

McCall and Coover[32] described a method for the preparation of copolymers of ethylene and β-propiolactone containing 2.8 wt. % of the lactone. The copolymerisation was performed in the presence of di-t-butyl peroxide.

The copolymerisation of styrene with β-propiolactone in the presence of radical initiators led to the formation of block-copolymers with terminal hydroxy- and carbonyl groups[33].

It is noteworthy that in all the studies enumerated above there are no direct data demonstrating that the addition of cyclic compounds to the growing polymeric molecule takes place via ring opening by a radical mechanism. In general the radical copolymerisation of vinyl monomers with cyclic compounds takes place with difficulty. However, in special cases the process does occur and leads to the formation of copolymers with alternating units of the initial monomer. For example, Hauptschein and Lesser[34] achieved the radical copolymerisation of perfluoropropene with epoxyethane (both with initiation by ultraviolet light and in the presence of di-t-butyl peroxide), the monomer ratio in the initial mixture being varied from 1 : 1 to 2 : 1. In all cases polymeric products were obtained in the form of a thick viscous mass with high stability to the action of chemical reagents. The stability of this copolymer to the action of concentrated sulphuric acid and heating with 47% hydriodic acid for 24 h at 150°C suggests that the reaction product is a copolymer with alternating units of the initial monomers in proportions of 1 : 1, since otherwise it would have decomposed. Probably the chain of this copolymer is constructed on the "head to tail" principle, i.e. $-(C_3F_6-O-CH_2-CH_2-)$. Copolymers of epoxyethane with trifluoroethylene were obtained similarly. Vinylidene fluoride does not form copolymers with epoxyethane but the rate of homopolymerisation of vinylidene fluoride in the presence of epoxyethane is much higher.

Spirodi-*o*-xylylene may be quoted as a specific cyclic monomer, which in the presence of radical initiators is capable of homopolymerisation and copolymerisation with a number of olefins (styrene, acrylates, and methacrylates); its copolymerisation with many olefins yields copolymers with a 1 : 1 ratio of structural units[35]:



A distinct feature of this monomer is the presence of a double bond conjugated with the ring. This double bond evidently makes the monomer sensitive to radical initiators. In this case polymerisation takes place with the opening of the double bond and the conjugated ring, as in the polymerisation of conjugated dienes by 1,4-addition. 1,1-Dichloro-2-vinylcyclopropane[36] and vinylcyclopropane[37] polymerise in the same way, under the action of both cationic and radical catalysts.

III. COPOLYMERISATION OF CYCLIC COMPOUNDS

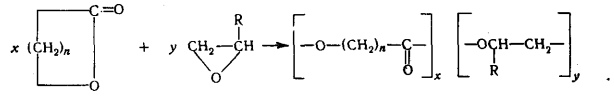
The copolymerisation of cyclic monomers can be used for the preparation of various classes of linear hetero-chain copolymers, which can find a wide variety of applications. Most of the studies which have been made dealt with the copolymerisation of cyclic compounds of the same chemical type, differing from one another only in the number of units in the ring or the presence of various substituents. A number of investigations have been made of the copolymerisation of lactams[41–45] and lactones[46,47]. The copolymerisation of various cyclic ethers has been discussed in detail in the monograph of Furukawa and Saegusa[48].

The present review deals with studies on the polymerisation of cyclic compounds of different chemical types. Copolymers with hetero-bonds in the macromolecular chain derived from both copolymerising monomers can be obtained in such copolymerisation. However, the number of studies on this type of copolymerisation is small and covers a very restricted range of monomers (Table 2).

1. Copolymerisation of Lactones

a. Copolymerisation with oxygen-containing compounds. Lactones can polymerise with cyclic ethers (epoxyalkanes, tetrahydrofuran, oxetans, trioxan), imines, and certain other cyclic compounds. The activity of lactones in the copolymerisation reaction is different and depends on the structure of the lactone, the chemical type and structure of the second co-monomer, and the catalytic system used.

The copolymerisation of lactones with epoxy-compounds should lead to the formation of copolymers containing ether and ester links in the chain:



This process has attracted the attention of many investigators, but satisfactory results cannot be always achieved. Thus Furukawa and coworkers[78] established that, when cadmium, zinc, or aluminium alkyls are used as catalysts

and oxygen, water, or alcohol as co-catalysts (i.e. catalytic systems which are fairly effective for the homopolymerisation of β-propiolactone[78] and epoxypropane[79]) in the copolymerisation of β-propiolactone with epoxypropane, a copolymer does not form. Catalytic systems such as boron trifluoride-ether and triethylaluminium with added water also proved to be ineffective[49]. A copolymer of β-propiolactone and epoxypropane could be obtained only in the presence of aluminium tri-isopropoxide but with a very low (up to 5%) content of epoxypropane units[49]. Cherdron and Ohse[50] also failed when they used organoaluminium compounds and boron trifluoride-ether as catalysts for this copolymerisation. Thus it is evident that the copolymerisation of β-propiolactone with epoxypropane in the presence of the above catalysts either does not take place at all or takes place with great difficulty.

In contrast to epoxypropane, other epoxy-compounds (epichlorohydrin, styrene oxide) undergo copolymerisation with β-propiolactone much more readily. The copolymerisation of β-propiolactone with epichlorohydrin[49,50] and styrene oxide[50] takes place readily in the presence of triethylaluminium, but boron trifluoride-ether and aluminium tri-isopropoxide proved to be ineffective as catalysts of the copolymerisation of epichlorohydrin with β-propiolactone[49].

In contrast to β-propiolactone, δ-valerolactone copolymerises comparatively readily with epoxypropane and styrene oxide in the presence of triethylaluminium or boron trifluoride-ether.

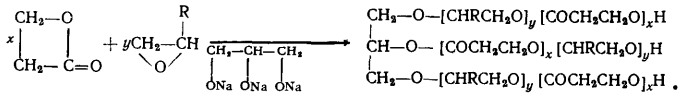
As a rule, the copolymers of lactones with epoxy-compounds are solid crystalline products with a molecular weight of several tens of thousands and with a melting point lower than those of the corresponding lactone-homopolymers. However, the use of polyhydric alcohols or the corresponding alkoxides as polyfunctional co-catalysts in the copolymerisation of lactones with epoxy-compounds leads to the formation of branched-chain liquid copolymers

Table 2. Copolymerisation of cyclic compounds.

Co-monomers	Type of catalyst: anionic	Type of catalyst: cationic	Refs.
β-Propiolactone–			
–epoxypropane	aluminium tri-iso-propoxide	–	49
–epichlorohydrin	triethylaluminium	BF_3-ether	49, 50
–styrene oxide	ditto	ditto	50
–butadiene monoxide	"	"	50
–isoprene monoxide	"	"	50
–allylglycidic ether	"	"	50
–vinylcyclohexene monoxide	"	"	50
–trioxan	–	"	50
–3,3-bis(chloromethyl)oxacyclobutane	triethylaluminium–water	"	52–54
–tetrahydrofuran	ditto	"	49
–aziridine	triethylamine	BF_3-ether, stannic chloride	55,56
–*N*-carboxy-anhydride of DL-valine	pyridine, sodium methoxide	–	57, 58
–phenyl ester of ethylene phosphorous acid	tertiary amines, alkali metal alkoxides	–	59
ββ-Dimethyl-β-propiolactone			
–3,3-bis(chloromethyl)oxacyclobutane	–	BF_3-ether	54
β-Methyl-β-propiolactone–			
–3,3-bis(chloromethyl)-oxacyclobutane	–	ditto	54
α-Methyl-β-propiolactone–			
–3,3-bis(chloromethyl)-oxacyclobutane	–	"	54
αα-Dimethyl-β-propiolactone–			
–3,3-bis(chloromethyl)-oxacyclobutane	–	"	54
γ-Butyrolactone–			
–trioxan	–	"	60
–aziridine	triethylamine	BF_3-ether, stannic chloride	55
δ-Valerolactone–			
–epoxypropane	triethylaluminium	BF_3-ether	50
–styrene oxide	ditto	ditto	50
ε-Caprolactone–			
–aziridine	triethylamine	BF_3-ether, stannic chloride	55
–ε-caprolactam	tri-isobutylaluminium, sodium	–	61
Aziridine–			
–ethylene carbonate*	–	–	62
–succinimide*	–	–	63
–glutarimide	–	BF_3-ether	63
–phthalimide	–	ditto	63
–epoxypropane	–	"	64–66
2-Methylaziridine–			
–succinimide	–	"	63
N-Butylaziridine–			
–phthalic anhydride*	–	–	67
N-Cyclohexylaziridine–			
–phthalic anhydride*	–	–	67
Succinic anhydride–			
–3-phenyl-2-oxazolidinone	lithium chloride, benzonitrile, tetraethylammonium chloride	*p*-toluenesulphonic acid, succinic acid, titanium tetrachloride	68
–5-phenoxymethyl-3-phenyl-2-oxazolidinone	ditto	ditto	68
–3,5-diphenyl-2-oxazolidinone	"	"	68
Phthalic anhydride–			
–epoxyethane	benzyldimethylamine	–	69
–epoxypropane	butyl-lithium, ethylmagnesium bromide, diethylmagnesium, diethylzinc, diethylcadmium	–	70
–epichlorohydrin	benzyldimethylamine	–	69
–epoxycyclohexane	ditto	–	69
–allylglycidic ether	"	–	69
–3-phenyl-2-oxazolidinone	lithium chloride, benzonitrile, tetraethylammonium chloride	*p*-toluene sulphonic acid, succinic acid, titanium tetrachloride	68
–5-phenoxymethyl-3-phenyl-2-oxazolidinone	ditto	ditto	68
–3,5-diphenyl-2-oxazolidinone	"	"	68
Tetrachlorophthalic anhydride–			
–butylglycidic ether	–	zinc chloride	71
Mixture of maleic and phthalic anhydrides–			
–epoxypropane	tetramethyleneammonium bromide, lithium chloride	–	72
Pyromellitic anhydride–			
–epichlorohydrin	triethylaluminium, lithium chloride, benzyldimethylamine	–	73
–phenylglycidic ether	ditto	–	73
–3,3-bis(chloromethyl)-oxacyclobutane	"	–	73
3-Phenyl-Δ⁴-tetrahydrophthalic anhydride–			
–epoxypropane	diethylzinc–(+)borneol	–	74
Epoxypropane–			
–propylene sulphide	alkali metal hydroxides	–	75
–butylene sulphide	–	complexes of iron chlorides with epoxypropane	76
–*N*-carboxy-anhydride of DL-alanine	triethylaluminium, diethylzinc, diethylzinc–water (alcohol), triethylaluminium–water, aluminium tri-isopropoxide, sodium methoxide, and diethylamine	–	77

* Without catalyst.

with terminal hydroxyls[50], which gives rise to wide opportunities for the modification of such copolymers by allowing them to react with isocyanates and other compounds:



Cherdron and Ohse[50] also studied the copolymerisation of lactones with epoxy-compounds containing unsaturated bonds. These were butadiene monoxide [epoxybutene ? (Ed. of Translation)], isoprene monoxide, allylglycidyl ether, and vinylcyclohexene monoxide. It was established that unsaturated epoxy-compounds which polymerise with difficulty via ring opening are also difficult to copolymerise with a lactone. The first three epoxy-compounds belong to this class. Vinylcyclohexene monoxide, which itself readily polymerises, is also easy to copolymerise with lactones. It is noteworthy that the choice of catalyst influences to a high degree the composition and properties of the copolymers formed. In the presence of boron trifluoride-ether liquid copolymers of β-propiolactone and vinylcyclohexene monoxide enriched in the second component are produced. On the other hand, in the copolymerisation of the same compounds in the presence of triethylaluminium solid copolymers enriched in β-propiolactone residues are produced. The presence of double bonds in such copolymers gives rise to the possibility of their further modification. For example, when the unsaturated epoxy-compound is copolymerised with a lactone in the presence of triethylaluminium in styrene, which does not polymerise under the influence of triethylaluminium without a co-catalyst, it is possible to achieve two-stage copolymerisation[50]. The first stage involves the formation of the copolymer of the lactone with the unsaturated epoxy-compound, and, after the addition of a radical initiator to the reaction mixture, the copolymerisation of styrene with the copolymer takes place.

Toda et al.[52,53] investigated the copolymerisation of β-propiolactone with 3,3-bis(chloromethyl)oxacyclobutane in the presence of "triethylaluminium–water" and boron trifluoride-ether catalytic systems. In both cases copolymers insoluble in chloroform were obtained. The formation of a copolymer was confirmed by infrared spectroscopy. With increasing content of lactone in the initial mixture, the degree of conversion and the fraction insoluble in chloroform decrease. When the initial mixture contains 75 mole % of 3,3-bis(chloromethyl)oxacyclobutane, only the homopolymer of the latter is formed. The composition of the copolymer depends to a large extent on the type of catalyst used in the copolymerisation. The copolymers obtained in the presence of triethylaluminium and water contain more lactone units than those produced in the presence of boron trifluoride-ether.

Tsuda et al.[54] studied the effect of substituents on the reactivity of lactones in cationic copolymerisation with 3,3-bis(chloromethyl)-oxacyclobutane. The activity of the lactone investigated, found from the composition of the copolymers, decreases in the following sequence: $\beta\beta$-dimethyl-β-propiolactone $\gg$ β-methyl-β-propiolactone $>$ β-propiolactone $>$ α-methyl-β-propiolactone $>$ $\alpha\beta$-dimethyl-β-propiolactone. The authors[54] believe that in the polymerisation of β-lactones the C–O bond dissociates on the side of the carbonyl group except in $\beta\beta$-dimethylpropiolactone where it dissociates on the side of the alkyl groups.

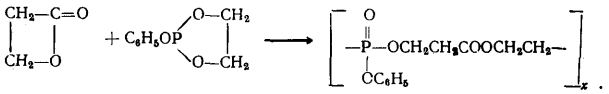
The copolymerisation of lactones with tetrahydrofuran[49] and trioxan[60] is also possible. Copolymers of tetrahydrofuran and β-propiolactone[50] have been obtained in the presence of the "triethylaluminium–water" catalytic system in the form of viscous liquids or resins. Trioxan has been copolymerised with γ-butyrolactam in the presence of boron trifluoride-ether[60].

Table 3 presents the copolymerisation constants of lactones and a series of cyclic ethers. The reactivity of the compounds undergoing copolymerisation, listed in Table 3, depends to some extent on the copolymerisation conditions: the nature of the catalyst, reaction temperature, etc.

Table 3. Constants for the copolymerisation of lactones with certain other cyclic compounds.

Copolymerising monomers		Copolymerisation constants		Catalyst	Refs.
1	2	r_1	r_2		
β-Propiolactone	styrene oxide	15.0	0.1±0.1	$Al(C_2H_5)_3$	50
ditto	epichlorohydrin	9.0	0.2±0.1	$Al(C_2H_5)_3$	50
"	tetrahydrofuran	0.4	2.9	$BF_3(C_2H_5)_2O$	49
"	ditto	0.1	5.5	$Al(C_2H_5)_3 - H_2O$	49
"	3,3-bis-(chloromethyl)oxacyclobutane	0.06	38	$BF_3(C_2H_5)_2O$ (at 0°)	52.53
"	ditto	0.04	30	$Al(C_2H_5)_3 - H_2O$ (at 0°)	52.53
"	"	0.05	16	$BF_3(C_2H_5)_2O$ (at −50°)	52.53
"	"	0.1	30	$Al(C_2H_5)_3 - H_2O$ (at −50°)	52.53
γ-Valerolactone	epichlorohydrin	5.3	0.25±0.1	$Al(C_2H_5)_3$	50

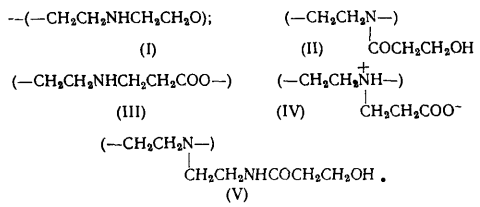
b. Copolymerisation of lactones with other cyclic compounds. Apart from the copolymerisation of lactones with cyclic ethers, cases are known where they were copolymerised with certain other cyclic compounds. The copolymerisation of lactones with cyclic phosphites is interesting[59]:



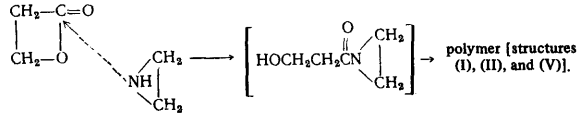
This results in the formation of a solid white polymer melting at 160°C. The reactions take place readily on heating (at or above 150°C) or even at room temperature in the presence of basic catalysts (tertiary amines, amides, alkali metal alkoxides, etc).

A few studies have been made on the copolymerisation of lactones with aziridines[55,56]. The copolymerisation of β-propiolactone, γ-butyrolactone, and ϵ-caprolactone with aziridine is catalysed by compounds such as boron trifluoride-ether, stannic chloride, triethylamine, sodium cyanide, and mercurous chloride[55]. Polymers with a low molecular weight were obtained in all cases. With increasing dielectric constants of the solvents in which the copolymerisation is carried out, there is an increase in the yield of copolymer. It is interesting to note that aziridine and β-propiolactone activate one another in the copolymerisation reaction and the latter can take place without catalysts[56]. The structure of the copolymer formed depends to a large extent on the dielectric constant of the solvent but is independent of the type of catalyst used[55,56]. On the basic of infrared spectroscopic data, the authors suggest that the formation of several different structures is possible

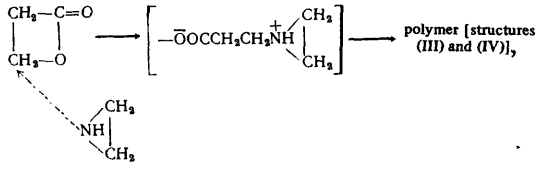
in the synthesis of the copolymer of β-propiolactone and aziridine:



The formation of a particular copolymer structure depends on the site of ring opening, which is in turn determined to a large extent by the polarity of the solvent used in the reaction. The role of the solvent as regards the variation of the site of ring opening is not entirely clear, but it may involve a change in the distribution of electron density of the monomer when the polar solvent adds to the carbonyl carbon of the lactone. In non-polar solvents the carbonyl carbon of the lactone is probably attacked by the nitrogen atom of aziridine:



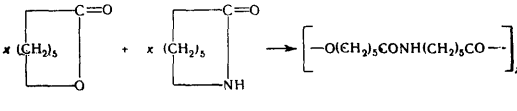
Here too copolymers with structure (I), (II), or (V) are formed. On the other hand, in polar solvents aziridine may attack the β-carbon atom of the lactone:



which results in the formation of copolymers with structures (III) and (IV).

Dermer and Ames[57,58] achieved the copolymerisation of β-propiolactone with the *N*-carboxy-anhydride of DL-valine in a mixture of anisole and benzene in the presence of pyridine and obtained a low-molecular copolymer (mol. wt. about 1150) in the form of a white powder with a softening temperature of 20°C. When the same reactants were copolymerised in the presence of sodium methoxide, it proved possible to increase somewhat both the molecular weight (about 3550) and the softening temperature of the copolymer (85°C).[57]

An interesting method for the preparation of polyamidoethers consists in the copolymerisation of ε-caprolactone with ε-caprolactam in the presence of tri-isobutylaluminium or sodium as catalysts[61]:

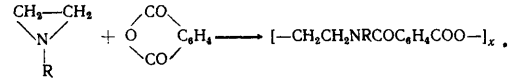


Thus lactones are capable of forming copolymers with a number of cyclic compounds; at the present time the copolymerisation of lactones with cyclic oxygen-containing compounds has been investigated in greatest detail.

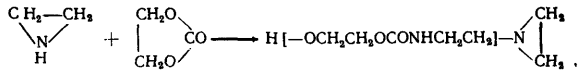
2. Copolymerisation of Aziridines

The copolymerisation of aziridine with lactones was described in the previous section[55,56]. Apart from this, examples of the copolymerisation of aziridines with certain other cyclic compounds are known.

N-Substituted polyamidoethers are formed in the copolymerisation of *N*-substituted aziridines (*N*-butylaziridine, *N*-cyclohexylaziridine) with dibasic acid anhydrides[67]:

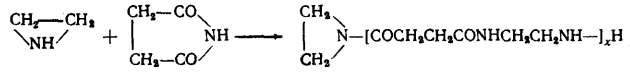


The copolymerisation of aziridines with cyclic carbonates leads to the formation of high-molecular polyurethanes with terminal hydroxy- and alkylimino-groups:



Copolymers with a degree of polymerisation up to 2000 have been obtained in the copolymerisation of aziridine with ethylene carbonate[62]. In both cases described above the copolymerisation was carried out by heating the initial monomers without any catalysts.

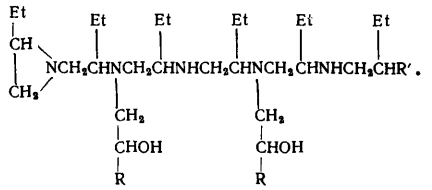
The copolymerisation of aziridines with cyclic imides, which leads to the formation of crystalline polyamides, is an interesting reaction[63]. Thus the copolymerisation of aziridine and succinimide yields a polyamide melting at about 300°C:



This reaction takes place particularly readily with compounds having small rings and constitutes an interesting method for the preparation of polyamides with short methylene chains. Crystalline polyamides have been obtained in the copolymerisation of the following monomer systems: 2-methylaziridine–succinimide, aziridine–glutarimide, and aziridine–phthalimide. The reactivity of imides in copolymerisation with ethyleneimine decreases in the following sequence: maleimide > phthalimide > succinimide > glutarimide > *N*-methylsuccinimide[63]. The copolymerisation of aziridines with imides can be carried out both with and without catalysts by heating the initial monomers. The presence of boron trifluoride-ether as catalyst for the copolymerisation of aziridines with cyclic imides favours the formation of a copolymer enriched in aziridine units, while the addition of triethylamine does not affect the composition of the copolymer[63].

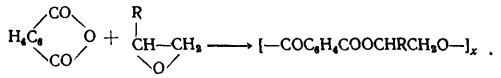
The copolymerisation of aziridines with epoxyalkanes has been described[64,80,81]. However, Overberger and Tobkes[65] have shown that the resulting copolymerisation products have a complex structure. In the copolymerisation of 2-ethylaziridine with 1,2-epoxy-compounds, they used Lewis acids as catalysts. In the presence of the most active catalyst, boron trifluoride-ether, copolymers with a polyimine structure are formed, in which the imino-groups are β-hydroxyalkylated by the 1,2-epoxy-compounds. Under the copolymerisation conditions investigated, the imine is more active than the epoxy-compound. Probably the polyimine chain grows to a considerable length before the epoxyalkane units are incorporated into it. The authors suggest that in the first stages of the copolymerisation, complexes of the catalysts with the imine residues of the

polymer are mainly formed, as a result of which the catalyst is incapable of inducing the polymerisation of the epoxy-compound. The authors attribute the following structure to the copolymer of 2-ethylaziridine and epoxydodecane:



3. Copolymerisation of Anhydrides

The copolymerisation of dicarboxylic acid anhydrides with epoxyalkanes leading to the formation of polyesters has been comparatively well investigated:

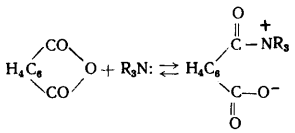


Fish and Hoffman[82-84] established that, in the copolymerisation of epoxy-compounds with anhydrides in the absence of catalysts, the epoxy-compounds are partially homopolymerised. In order to reduce the degree of homopolymerisation and to ensure more complete copolymerisation, the ratio of the anhydride to the epoxy-compound should be 0.85 : 1.[84,85]

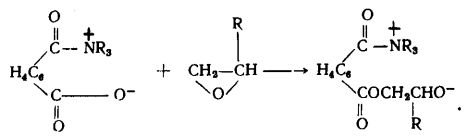
The use of catalysts favours the formation of polyesters. Fisher[69] showed that the polyesterification of dibasic acid anhydrides with epoxy-compounds in the presence of tertiary amines as catalysts takes place to the extent of 98–99% and the molecular weight of the polymers formed reaches about 18 500. The properties of the polyesters depend on the structure of the starting materials. The copolymerisation of epoxyethane with various anhydrides yields highly crystalline polymers which melt in the range 110–165 °C depending on the structure of the anhydride. The copolymerisation of epoxycyclohexane with anhydride yields polyesters melting above 100 °C. Structured polyesters are obtained in the copolymerisation of epoxy-compounds with maleic anhydride[71].

Fisher[69] proposed the following mechanism for the formation of polyesters in the copolymerisation of anhydrides with epoxy-compounds in the presence of amine catalysts.

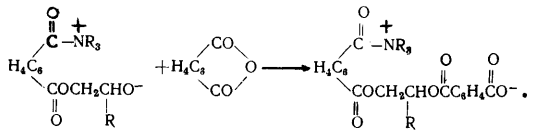
1. Activation of the anhydride by the amine with formation of a carboxylate anion:



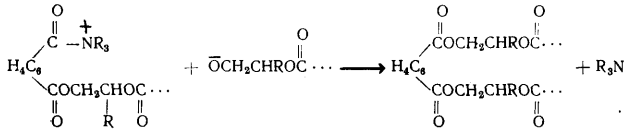
2. Reaction of the carboxylate anion formed with the epoxy-compound to form an alkoxide anion:



3. Reaction of the alkoxide anion with the anhydride:



In addition, growth of the polymeric chain is possible also when the amine is replaced by an alkoxide ion:

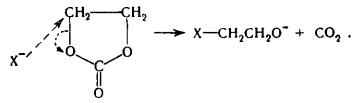


For the preparation of polyesters by the copolymerisation of cyclic compounds, one can use instead of epoxy-compounds the esters of dihydric alcohols and carbonic or sulphurous acids which have a cyclic structure and which are converted at high temperatures into epoxy-compounds with evolution of carbon monoxide or sulphur dioxide[86,87]. In this case polyesters are readily synthesised in the presence of various catalysts (metal oxides, tetraethylammonium bromide, lithium chloride, alkali metal salts of organic and inorganic acids). Schwenk et al.[86] obtained by this method polyesters with molecular weights up to 90 000. The increase of the rate of copolymerisation with the polarity of the reaction medium at various monomer concentrations and also the fact that the initiator anions are incorporated into the polyester macromolecules during copolymerisation, and finally the termination of the growing chain by substances containing active hydrogen ions indicate an anionic copolymerisation mechanism[87]. Schwenk et al.[86] suggest the following mechanism for the formation of polyesters in the copolymerisation of dicarboxylic acid anhydrides with cyclic carbonates in the presence of salts of the type MX.

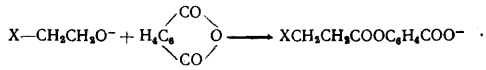
1. Initiation:



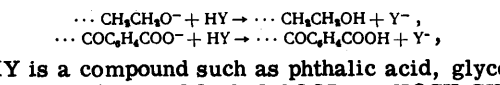
where MX is an alkali metal salt of an organic or inorganic acid;



2. Growth of the polymeric chain:



3. Chain termination:



where HY is a compound such as phthalic acid, glycol, or water and $Y^- = OH^-$, $HOOCC_6H_4COO^-$, or $HOCH_2CH_2O^-$.

Organometallic compounds, for example n-C_4H_9Li, C_2H_5MgBr, $(C_2H_5)_2Mg$, $(C_2H_5)_2Zn$, and $(C_2H_5)_2Cd$ are active catalysts of the reaction of epoxy-compounds with anhydrides[70]. In the presence of diethylzinc the copolymerisation of epoxypropane with anhydrides takes place at relatively low temperatures (about 30 °C). It has been established by infrared spectroscopy and elemental analysis that the copolymer obtained in the copolymerisation of epoxypropane and phthalic anhydride is a polyester with the structural formula $[-CH_2CH(CH_3)OCOC_6H_4COO-]_n$.[70]

Unsaturated polyesters are obtained in the copolymerisation of a mixture of maleic and phthalic anhydrides with epoxypropane in the presence of tetramethyleneammonium bromide or lithium chloride. The polyester formed contains unsaturated bonds and are capable of being modified chemically—for example, it can be copolymerised with styrenes[72].

The copolymerisation of pyromellitic anhydride with the glycidylphenyl ether leads to the formation of a ladder-type polymer in which two polyester chains are linked by bridges consisting of tetrasubstituted benzene rings. The copolymerisation was performed in dioxan in the presence of dimethylbenzylamine, lithium chloride, sodium acetate, sodium phthalate, and triethylaluminium. The first catalyst is the most effective. When the copolymerisation is carried out in dilute solutions, a soluble polyester is formed. Judging from infrared spectroscopic results, the polyester does not contain anhydride groups but its hydrolysis shows that the ratio of the anhydride and epoxy-units is greater than two, i.e. the polymer contains also ester units[73]. The copolymerisation of pyromellitic anhydride with epichlorohydrin and 3,3-bis(chloromethyl)oxetane has also been investigated[73].

The use of an asymmetric catalytic system in the copolymerisation of epoxy-compounds with anhydrides permits the synthesis of active copolymers from inactive monomers. Thus in the copolymerisation of (±)-epoxypropane with the optically inactive 3-phenyl-Δ^4-tetrahydrophthalic anhydride in the presence of the diethylzinc–(+)-borneol system a polyester was obtained which exhibited dextrorotatory optical activity in chloroform (70°).[74]

Branched-chain thermoplastic polyesters are formed in the copolymerisation of dicarboxylic acid anhydrides and epoxy-compounds in the presence of pentaerythritol[88].

4. Other Types of Copolymerisation

Above it was pointed out that epoxy-compounds can undergo copolymerisation with a number of other cyclic monomers (lactones, anhydrides, aziridines), forming copolymers of various types. In addition, there are several patents dealing with the copolymerisation of epoxyalkanes with alkylene sulphides. Alkali metal hydroxides[75] and complexes of $FeCl_2$ and $FeCl_3$ with the monomeric epoxy-compound[77] ($2FeCl_2.C_3H_6O$, $FeCl_3.2C_3H_6O$, and $FeCl_3.3C_3H_6O$) have been suggested as catalysts. In the first case the products are copolymers of low molecular weight (200–1500) which are either mobile liquids or oils. Such copolymers show enhanced stability to oxidation and they are recommended as lubricating oils. In the presence of catalysts of the second type epoxypropane has been copolymerised with phenylethylene sulphide, 1,2-butylene sulphide, and propylene sulphide. Copolymers with a high molecular weight (up to 100 000), capable of forming films stable to the action of light and heat (in the absence of stabilisers) and with a relatively high strength (tensile strength 385 kg cm^{-2}) were obtained.

Tsuruta et al.[77] copolymerised epoxypropane with the *N*-carboxy-anhydride of DL-alanine. Diethylzinc and triethylaluminium are effective catalysts of this copolymerisation. The presence of co-catalysts (water or alcohol) lowers the yield of the copolymer. The main chain of the copolymer obtained probably contains ether, ester, amide, and urethane groups.

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At the present time it can be assumed that generally speaking all heterocycles with sufficiently polar bonds or bonds capable of polarisation under particular conditions can undergo polymerisation. Thermodynamic factors play the main role in carbocyclic compounds. However, the polymerisation conditions have been by no means always discovered and not all cyclic compounds could be polymerised.

Even greater difficulties are encountered in copolymerisation. Even among compounds of the same type, the capacity for polymerisation can differ significantly, which makes copolymerisation difficult. On the other hand, for monomers of different types the determination of copolymerisation conditions is frequently very difficult.

Among the problems which arise in the copolymerisation of cyclic compounds, the following are particularly significant at the present time. Very often the molecular weight of the copolymers is lower than that of the corresponding homopolymers. This can be caused by a difference in the reactivity of the copolymerising compounds, as a result of which the chosen conditions are not altogether suitable for both monomers. The reaction conditions can be too mild for the successful polymerisation of one of the components or too severe, so that one monomer decomposes into substances which inhibit polymerisation. Thus the choice of process conditions is very important. In choosing the conditions for copolymerisation, it is necessary to make sure that they differ as little as possible from the polymerisation conditions of the individual monomers. For this reason the problems of catalysis are of primary importance.

Furthermore, considerable difficulties arise in connection with the very proof that copolymers are formed. In contrast to the copolymerisation of vinyl compounds, in the copolymerisation of monomers of different chemical types it is particularly important to prove the formation of copolymers, since under these conditions the homopolymerisation of one or other monomer takes place readily.

The question of the preparation of block copolymers, particularly those of a regular structure, is of great interest in connection with the copolymerisation of cyclic compounds, as for compounds of other types.

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Metal Ammonium Phosphates and Their New Applications

L.M.Lapina

The review deals with the methods of preparation and applications of double salts comprising metal and ammonium phosphates. Particular attention has been given to the methods of preparation and properties of divalent metal compounds of composition $MNH_4PO_4.nH_2O$ which are interesting as complex, long-acting fertilizers.
The syntheses and investigations of those trivalent metal compounds which can be formed on interaction between water-soluble phosphorus fertilizers and soils are described extensively. The bibliography comprises 65 references.

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I. INTRODUCTION

Metal ammonium phosphates include a wide range of compounds which can be denoted by the common formula $a(NH_4)_2O.bMO.cP_2O_5.nH_2O$, where M is a divalent metal, and $a(NH_4)_2O.M_2O_3.cP_2O_5.nH_2O$, where M is a trivalent metal†.

Many of these compounds were already known in the 19th century. Compounds of the type $MNH_4PO_4.nH_2O$, which have found application in analytical chemistry, have been most thoroughly investigated. For example, the determination of phosphorus and magnesium is based on the isolation of $MgNH_4PO_4.6H_2O$, which is then converted to pyrophosphate by heat treatment, and the isolation of $ZnNH_4PO_4$, $MnNH_4PO_4.H_2O$, and $CdNH_4PO_4.H_2O$ constitutes the basis of the determination of the corresponding metals.

Recently the applications of these compounds have greatly increased. In particular investigators in the field of fertilizers have drawn attention to the fact that certain compounds of the type $MNH_4PO_4.nH_2O$ can be used as complex fertilizers containing three nutrient elements: nitrogen, phosphorus, and the corresponding metal (magnesium, manganese, zinc, copper, etc.). Copper, manganese, and zinc are required by plants in micro-amounts, while magnesium is required in comparatively large quantities.

Technological procedures for the preparation of magnesium, zinc, and iron ammonium phosphates have been developed at the Institute of Fertilizers, Insecticides, and Fungicides (NIUIF).[1] Magnesium ammonium phosphate monohydrate‡ was tested under field conditions on different crops and yielded positive results[2]. Manganese, copper, and zinc ammonium phosphates were subjected to vegetative tests and proved to be fairly effective under many conditions.

American workers showed[3] that the high assimilability of metal ammonium phosphates by plants can be explained by the rapid nitrification of their nitrogen content by soil bacteria, as a result of which the salt molecule breaks down and all the components become available to the plant.

At the beginning of the 1960's Grace and Co. in the USA[4,5] announced the manufacture and application as fertilizers of magnesium ammonium phosphate and certain other similar compounds. This communication was followed by a paper dealing with the study of the properties and tests of these fertilizers[3].

The bright colour of certain of the divalent metal compounds has led to their employment (mainly cobalt ammonium phosphate) as pigments in artists paints[6,7].

Iron ammonium phosphate and manganese ammonium phosphate have been suggested as components of priming paints in anti-corrosion coatings[6,8], since, apart from their other valuable properties, they behave as acceptors of acids and oxygen, whereby they prevent corrosion.

The method of extraction of doubly charged metal cations[9], in particular calcium and magnesium, from sea water to prevent the formation of scale is based on metal ammonium phosphates. In this procedure phosphoric acid and ammonia are added to sea water and the metal ammonium phosphates formed are used as fertilizers.

Salutsky and Dunseth[10] believe it to be more useful to extract cations such as Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, and Ca^{2+} from salt solutions of various types, including sea water, by passing them through a layer of $MgNH_4PO_4.H_2O$, where magnesium ions are replaced by the above cations.

† Compounds in which the ammonium ion is replaced by a monovalent metal (sodium, potassium, lithium) are also very widespread but these will be mentioned only incidentally.

‡ $MgNH_4PO_4.6H_2O$ is of no interest as a fertilizer, since it is unstable and contains a smaller percentage of nutrient substances than $MgNH_4PO_4.H_2O$.