U. D. C. 547.476.2

Polymerisation of Lactones

Yu.N.Sazanov

This is a review of investigations on the polymerisation of lactones. The author briefly touches on the history of the subject, the advantage of the synthesis of polyesters by the method of polymerisation over polycondensation, and the essential nomenclature of lactones. The polymerisation of β-, γ-, and δ-lactones, both unsubstituted and with various substituents, in the presence of anionic and cationic catalysts, and also under the action of ionising radiation, is considered in detail. Conditions and possible schemes of mechanism for the polymerisation of these lactones, and also the effect of substituents on the course of the process, are given. Examples of the copolymerisation of this class of compounds with either vinyl or cyclic monomers are considered separately. The available published data on the physicochemical properties of polyesters synthesised from lactones and their applications as fibre- or film-forming polymers is presented. Bibliography of 80 references.

CONTENTS

I. Introduction 463
II. Polymerisation of β-lactones 463
III. Polymerisation of γ- and δ-lactones 466
IV. Copolymerisation of lactones 467

I. INTRODUCTION

The first communications on the polymerisation of lactones date from 1903, when Fichter and Beisswenger[1] and later Hollo[2] obtained from liquid monomeric δ-valerolactone a waxy crystalline mass, m.p. 47–48°C. Carothers and coworkers[3] showed that a mixture of oligomers with $M = 3000–4000$ is formed.

Great attention is now being paid to the polymerisation of oxygen-containing cyclic esters, especially lactones. The formation of polyesters in this manner has considerable advantages over polycondensation. Firstly, the process can be carried out under milder conditions, at negative or near-room temperatures; secondly, the need for removing side-products disappears, which is not true for polycondensation. These advantages enable polyesters of high molecular weight which exhibit a series of valuable physicochemical properties and are suitable for the preparation of high-quality fibres and films to be obtained.

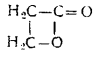
Lactones are polymerised in the presence of acid and basic catalysts, complex catalysts, and under the action of ionising radiations. They are not polymerised by a radical mechanism.

There is some confusion in the literature concerning the terminology of lactones. Usually the name of a lactone is derived from the name of the acid on the basis of which it is constructed, but some authors name the lactone by starting from the total number of carbon atoms entering into the lactone, and others, from the number of carbon atoms forming the lactone ring. We think that the second principle of classification is the more rigorous and subsequently will adhere to the following nomenclature: four-membered lactone, β-propiolactone; five-membered γ-butyrolactone; six-membered, δ-valerolactone; seven-membered, ε-caprolactone. The positions of the substituents at carbon atoms of the lactone ring will be shown by starting the numbering from the carbonyl-carbon.

II. POLYMERISATION OF β-LACTONES

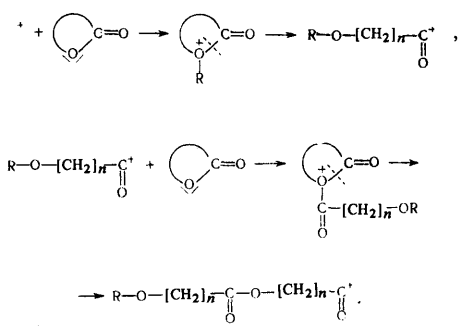
1. Unsubstituted β-Lactones

One of the most studied representatives of the class of lactones is β-propiolactone:



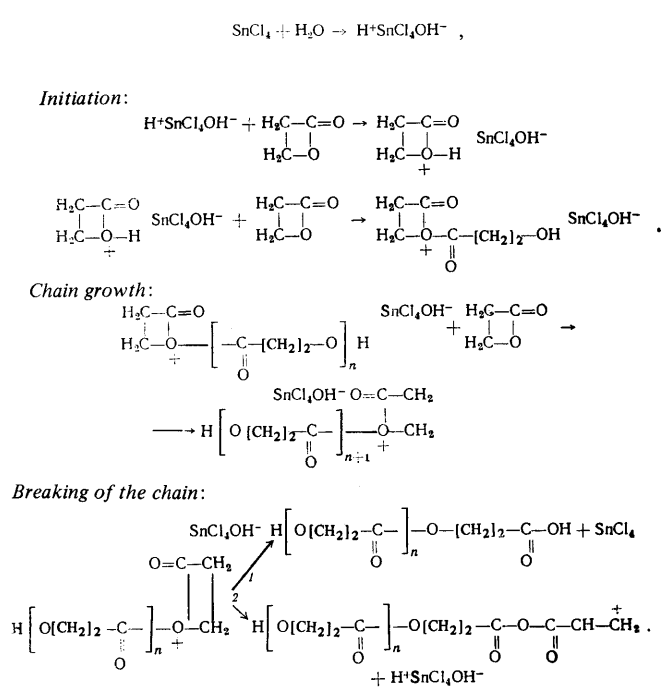
The reactions of β-propiolactone with various organic and inorganic compounds were investigated in detail by Gresham and coworkers[4–15].

Cationic polarisation. In 1948 Gresham and coworkers[6] first described the formation of a polymer with $M = 800–1000$ in the reaction of β-propiolactone with conc. H_2SO_4 or $FeCl_3$. In 1962, Cherdron and coworkers[17] investigated the polymerisation of β-propiolactone in the presence of $AlCl_3$ and acetyl perchlorate. The initial β-propiolactone was distilled in thoroughly dried apparatus under a vacuum in the presence of 2% tolylene di-isocyanate. The purity of the product was checked by gas chromatography and from the stability of the monomer on storage (at a temperature $\gtrsim 60°C$). The polymerisation was carried out at 20°C without solvent under an atmosphere of nitrogen in the presence of the above catalysts, in 1×10^{-3} M concentration. The polymers obtained had a polyester structure with $M \simeq 100\,000$. The following mechanism was proposed for the cationic polymerisation of lactones:



Yamashita and coworkers[18] carried out the polymerisation of β-propiolactone in the presence of conc. H_2SO_4 and also Lewis acids ($FeCl_3$, $SnCl_4$, $AlCl_3$, $ZnCl_2$, and BF_3. ether) at 0° and 20°C for a long time (24 h to 5 months). Low-molecular weight polymers were obtained ($\eta_{sp}/c = 0.05$) with m.p. 76–80°C. Polymers are not formed in the presence of $ZnCl_2$ and $HgCl_2$. On the basis of the infrared

spectra and the terminal groups of the polymers the following mechanism of polymerisation in the presence of the $SnCl_4$–H_2O system was proposed:



The first mechanism of chain rupture mainly prevails, but at elevated temperatures the second reaction is also possible. In another study [19] Yamashita states that the principal reason for the breaking of the chain is the presence in the reaction system of negligible amounts of water. Recently, patents [20,21] and a paper [22] have appeared dealing with the polymerisation of β-propiolactone in the presence of Ti, Zr, and V phosphates. The polymers obtained had $[\eta]$ from 1 to 5.

Anionic Polymerisation. There have been more studies of the anionic polymerisation of β-propiolactone than of its cationic polymerisation. This is due to the principal possibility of carrying out the process in the presence of a series of catalytic systems without breaking of the chain and this in turn leads to the preparation of polymers with a higher molecular weight.

Gresham and coworkers [16] were the first to find that a low-molecular-weight product is formed by the action of NaOH on β-propiolactone, In continuing the work on the polymerisation of cyclic esters, Furukawa and coworkers [23,24] tested a series of organometallic compounds as catalysts for the polymerisation of β-propiolactone. These compounds are used both in the pure state and with cocatalysts. Low-molecular-weight polymers with $[\eta] < 0.2$ were synthesised.

Unlike the Japanese investigators, Cherdron and coworkers [25] found that thoroughly purified β-propiolactone in the presence of anionic catalysts gives high-molecular-weight polymers even at room temperature. Under the action of sodionaphthalene in dioxan solution at 100°C a polymer with $[\eta] \simeq 3$ is formed, but on polymerisation in the presence of aluminium alkyls products with M = 70 000–100 000 are obtained without cocatalysts. Use of water as cocatalyst leads to a considerable increase in the molecular weight of the polyester in accordance with the ratio of aluminium alkyl (or halogenoalkylaluminium) to water.

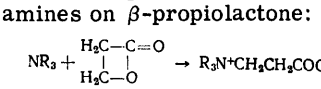
In their discussion of the mechanism of the anionic polymerisation the authors consider that, just as in the cationic process, the opening of the lactone ring takes place at the acyl bond, at which a negative charge passes from the initiator to the oxygen atom of the ring, which then reacts with a new molecule of the monomer.

Japanese investigators [18,19,22,26–28] tested a large number of inorganic and organic compounds of basic nature as catalysts for the polymerisation of β-propiolactone (Table 1). Of the compounds examined, the most effective catalysts are betaine, pyridine, and pyridine derivatives. Kagiya and coworkers [27,29] studied the polymerisation of β-propiolactone in the presence of pyridine and tried to relate the process determining the rate of reaction, the molecular weights, and the yield of polymers to the concentrations of the monomer and catalyst, the temperature, and the polymerisation time. The variation of the rate of the process with the ratio of monomer to catalyst is expressed by a curve with a maximum. On carrying out the reaction in a solvent, the activity of the catalyst increases with the dielectric strength of the medium and the monomer concentration. The scheme of the process is analogous to that of anionic polymerisation proposed earlier [25], with the addition of possible variants in the chain breaking and transfer.

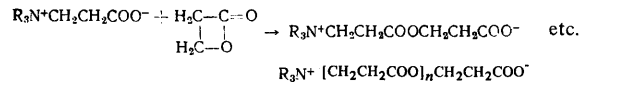
Table 1. Polymerisation of β-propiolactone in the presence of various anionic catalysts.

Catalyst, class of compound, and example	Conditions of reaction			Yield, %	η	Reference
	Temp., °C	Time, h	concn. of catalyst, mole per mole monomer			
Metal hydroxides (calcium, potassium, barium)	0—80	1—360	10^{-2}	70—90	0.1—0.5	22,26,28
Salts (potassium, sodium, or rubidium carbonates, etc.)	30	72—600	0.5—$2\cdot10^{-2}$	20—70	0.4	22,26,28
Alkoxides (sodium ethoxide, magnesium isopropoxide)	15	1000	0.3—$3\cdot10^{-3}$	50—70	0.4—0.6	19
Organic bases (triethylamine, betaine, pyridine, alkaloids)	0—25	200—800	$4\cdot10^{-3}$	70—90	0.5—1	19,22,27

In 1963 Etienne and Soulas [30] reported that in the presence of betaine β-propiolactone forms polymers of high molecular weight. It was noted earlier [31–33] that betaine or betaine-like complexes are formed by the action of tertiary amines on β-propiolactone:



which under appropriate conditions then leads to the polymerisation of β-propiolactone by the following scheme:



The authors of this scheme consider that the best catalyst of this type is the compound obtained in the reaction of a lactone and a tertiary amine; however, ordinary betaine (the internal salt of hydroxycarboxymethyltrimethylammonium or glycine trimethylbetaine) and glycine benzyldimethylbetaine are only slightly inferior. In the presence of these catalysts at a concentration of 0.1 mole % for 8–10 h at 15–20°C polymers of β-propiolactone with $[\eta] = 1.5$ were obtained. There is also a series of patents on the

polymerisation of β-propiolactone under the influence of organic compounds of the metals of Periodic Groups I and III,[34,35] alkalis on cotton wool[36] or wool[37], salts of Group I metals, and weak inorganic acids[38].

Polymerisation under the action of ionising radiations. Okamura and coworkers investigated the polymerisation of β-propiolactone under the action of γ-rays in the solid state[39-41] and in solution[42] at −78° and −196°C. Large and small crystals of β-propiolactone were irradiated (power of dose 10^3–10^6 roentgen h^{-1}). The products of highest molecular weight are formed from coarse crystals, hence the growth of the polymeric chain proceeds in a direction perpendicular to the long axis of the crystal monomer, and hence with increase in the size of the crystal the molecular weight of the polymer rises. At −78°C a crystalline polymer is formed even on irradiating fine crystals, but at −196°C an amorphous polymer is obtained. On the basis of X-ray investigations[39] and electron microscopy[40] it is suggested that the act of initiation takes place at the junctions of crystals and especially at places of crystal lattice defects. The yield of poly-β-propiolactam does not exceed 15–20%, $[\eta] = 0.15$–0.2, m.p. 110–120°C. In these studies the effect of post-polymerisation after cessation of the irradiation of the specimen is noted. The yield and viscosity of the polymer rise with increase in the dose power[43]. An anionic mechanism is proposed for the polymerisation of β-propiolactone under the action of γ-rays.

Apart from γ-irradiation, visible light in the presence of uranyl nitrate as an activator of the reaction[44], ultraviolet radiation[45], and beams of electrons with dose power 1.6×10^{-4}–20 Mrad min^{-1} [46] are also used for the initiation of the polymerisation of β-propiolactone, but only in the last instance could a polymer with $[\eta] = 1.4$–2.56 be isolated, though in very low yield. In the other instances low-molecular weight products were obtained in low yield.

Structure and properties of poly-β-propiolactone. Elemental analysis of the synthesised polymers and of the products of their acid and alkaline hydrolysis[18,26], chemical analysis of the terminal groups[17,18,25,47], infrared spectra[18,22,26,27,47,48] and the results of differential thermal analysis[22] show that the poly-β-propiolactone has the structure of a complex polyester, however, in connection with the absence of a common opinion about the site of the opening of the lactone ring during polymerisation there is still no definite conclusion concerning the regularity of the alternation of the links in the chain of the macromolecule. It is found, however, that the structure of the polyester obtained from the lactone differs from that of the polyester obtained in the polycondensation of diols and dicarboxylic acids[25].

In studying the infrared spectra of polymer films two types of structure were observed, the formation of which depends on the polymerisation conditions, particularly the nature of the catalyst[28]. However, the polymers of different structure did not exhibit differences in chemical properties and there were no differences in the infrared spectra of solutions of these polymers. The possibility of polymorphism of these polymers was suggested[47]. The existence of different crystal structures of poly-β-propiolactone was confirmed by Furukawa's investigations and also by Kagiya and coworkers[22]. Crystalline poly-β-propiolactone was obtained, which contained α and β forms with crystallisation temperatures of 65° and 20°C respectively and differed in X-ray diagrams and infrared spectra. It was found that the α form, with a repeat unit of 7.02 Å, has a 2_1 helical structure, whereas the β form, with repeat unit 4.28, has a planar zig-zag structure. The β form can be converted into the α by slow heating of a film of the polymer to 65°C. The β form is formed when the film is obtained from chloroform solution by slow evaporation; after rapid evaporation the α form predominates.

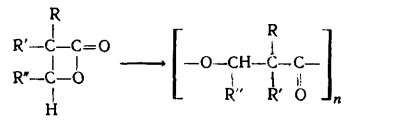
Similar investigations were made by Gianalvise[49], who determined, from the X-ray patterns of powders and fibres of poly-β-propiolactone, the repeat unit (6.02 Å) and also the unit-cell parameters and proposed the most probable helical structure of the macromolecule and its packing.

Poly-β-propiolactone is a mainly crystalline product with decomposition temperature 80–122°C and density from 1.2 to 1.4 (depending on the molecular weight). It is soluble in several organic solvents. According to the differential thermal analysis[22], the decomposition temperature of the polymer lies within the limits 230–250°C, but these values can be raised by increase in the molecular weight of the polymer. Owing to its low softening temperature poly-β-propiolactone is used as a modifier in natural fibres[36,37] or is mixed with other polymers which are more stable on heating.

2. Alkyl-Substituted β-Lactones

A patent[50] which appeared in 1960, and an article by the same authors[51] in 1962, described the production of polymers of a series of substituted β-propiolactones in the presence of triethylamine or triethylenediamine in bulk and in solution at 80–100°C. Some of the polymers obtained have high melting points (Table 2), and the lactones with a more symmetrical structure gave polymers with a higher molecular weight and which were more crystalline.

Table 2. Melting points of polymers of alkyl-substituted β-propiolactones.



Substituent			Melting point, °C
R	R′	R″	
CH_3	CH_3	H	240
CH_3	C_2H_5	H	125
CH_3	n-C_3H_7	H	80
CH_3	iso-C_3H_7	H	2[illegible]
CH_3	n-C_4H_9	H	liquid
CH_3	n-C_5H_{11}	H	54
C_2H_5	C_2H_5	H	226—245
C_2H_5	n-C_3H_7	H	200—205
C_2H_5	n-C_4H_9	H	179—180
n-C_3H_7	n-C_3H_7	H	257
n-C_3H_7	n-C_4H_9	H	227
n-C_4H_9	n-C_4H_9	H	245
—$[CH_2]_5$—		H	260—270
CH_3	CH_3	CH_3	185
CH_3	CH_3	C_2H_5	150

Most of the polymers synthesised are soluble in chlorine-containing solvents and form flexible transparent films which have a higher hydrolytic stability, and are more resistant to the action of HBr, dilute alkalis, and hydrazine solution than the polyesters obtained by polycondensation.

The polymerisation of $\alpha\alpha\beta$-trisubstituted lactones in the presence of betaine [30] is analogous to the polymerisation of the unsubstituted lactone [30], and the presence of alkyl substituents in the α position facilitates attack of the carbonyl carbon of the ring at the COO^- side of the anion and accelerates the polymerisation.

Yamashita and coworkers [18,26] carried out the polymerisation of α-methyl-, β-methyl, $\beta\beta$-dimethyl-, and β-isopropyl-β-propiolactones in the presence of anionic and cationic catalysts. All the polymers synthesised had low molecular weights ($[\eta] = 0.03-0.1$). The following series of activities of the β-propiolactones was compiled on the basis of the size of the molecular weight and the polymerisation times. In polymerisation in the presence of acid catalysts: $\beta\beta$-dimethyl > unsubstituted > α-methyl $\geqslant$ $\geqslant$ β-methyl > β-isopropyl; for basic catalysts: unsubstituted > α-methyl $\geqslant$ β-methyl > β-isopropyl > > $\beta\beta$-dimethyl. The polymerisation of $\alpha\alpha$-dimethyl-β-propiolactone [19] and $\beta\beta$-dimethyl-β-propiolactone [52] was investigated in greater detail. In the polymerisation of the former in the presence of CH_3CO_2K or KOH at 50°C high-molecular weight ($[\eta] = 1.7-2.6$) polymers, m.p. 230–240°C, were obtained in ~ 100% yield. The polymers are soluble in phenol, cresol, and trichloroacetic acid at elevated temperature. It was found that increasing the polymerisation time and also the $[M]/[C]$ ratio facilitates an increase in the degree of polymerisation. It was suggested that under these conditions "living polymers" are formed. In the polymerisation of $\alpha\alpha$-dimethyl-β-propiolactone in the presence of acid catalysts at 100°C only low-molecular-weight products are obtained. For the polymerisation of $\beta\beta$-dimethyl-β-propiolactone in the presence of $SbCl_5$, $SnCl_4$, and $ZnCl_2$ at 0°C polymers with $[\eta] = 0.08-0.12$ are formed after several days in yields of ~ 30%. When $Al(C_2H_5)_3$ or $Al(C_2H_5)_3-H_2O$ are used as catalysts under the same conditions polymers with a higher molecular weight ($[\eta] = 0.2-0.37$) are formed; however, in comparison with unsubstituted β-propiolactone and $\alpha\alpha$-dimethyl-β-propiolactone the activity of the β-substituted lactone during polymerisation is less. The reduction of activity is explained [52] firstly by the instability of the monomer itself at elevated temperature ($\beta\beta$-dimethyl-β-propiolactone readily decomposes into isobutene and CO_2), and secondly by the presence of a chain-transfer reaction, especially in the presence of cationic catalysts.

Interesting work on the determination of the activity of α-substituted β-propiolactones during polymerisation in the presence of basic catalysts, particularly pyridine, was begun by a group of Japanese investigators [53], who calculated, on the basis of the C–C "skeleton method" the delocalisation energy of the electrons in the lactone ring and also the frontal distribution of electron density as a function of the nature of the substituents at the carbon atoms of the lactone ring. Starting from the calculated values of the coulombic and resonance integrals, schemes of the frontal distribution of electron densities were drawn up for four types of α-substituted β-propiolactones and the following series of their polymerisation rates in decreasing order (substituents shown) given: $\alpha\alpha$-bis(chloromethyl) > α-chloromethyl-α-ethyl > α-chloromethyl-α-methyl > unsubstituted > $\alpha\alpha$-dimethyl.

3. Halogeno-substituted β-Lactones

Only a few papers have been published on the polymerisation of halogeno-substituted β-propiolactones and these deal only with the polymerisation conditions and certain properties of the polymers obtained. Thus in the polymerisation of $\alpha\alpha$-bischloromethyl-β-propiolactone [54] in the presence of powdered KOH for 6 h at 40–50°C a polymer with decomposition temperature ~ 300°C is obtained, from which fibres can be spun which exhibit a capability for cold drawing. On heating this monomer at 100–120°C for 5 h a polymer was obtained [55] with m.p. ~ 300°C, insoluble in most organic solvents and thermally stable at 230–250°C. A polymer of $\alpha\alpha$-bischloromethyl-β-propiolactone was obtained in the presence of KOH, triethylamine, and pyridine at 50°C. [56] Under these conditions $\beta\beta$-bischloromethyl-β-propiolactone was polymerised only in the presence of acid catalysts ($AlCl_3$, $SnCl_4$, BF_3.ether) and the above basic catalysts were ineffective [56]. The melting point of the polymer of $\beta\beta$-bischloromethyl-β-propiolactone is 150–160°C. Apart from the chloromethyl derivatives of β-propiolactone mention has been made of the production of polymers from $\alpha\alpha$-bisbromomethyl-, $\alpha\alpha$-bisfluoromethyl-, and α-bromomethyl-α-ethyl-β-propiolactones in the presence of triethylamine or triethylenediamine [51].

III. POLYMERISATION OF γ- AND δ-LACTONES

Nothing has been published on the production of homopolymers from γ-lactones, and only two papers have been published about the copolymerisation of γ-butyrolactone, which will be discussed below.

Six-membered or δ-valerolactones easily form polymers in the presence of ionic catalysts, sometimes even more easily [17,25] than β-lactones and polymers were first synthesised from lactones on the basis of δ-valerolactone [1,2]. Carothers and coworkers [3] obtained poly-δ-valerolactone with $M = \sim 4000$ by heating the monomer at 150°C in the presence of K_2CO_3 for 5 h. The polymers were waxy products with m.p. 53–55°C. Cherdron and coworkers [17,25] not only studied the polymerisation of β-propiolactone but also investigated the polymerisation of δ-valerolactone and ϵ-caprolactone. They proposed a mechanism of cationic and anionic polymerisation of these lactones analogous to the mechanism of cationic and anionic polymerisation of β-propiolactone with breaking of the acyl bond of the ring, in which the anionic mechanism differed from that proposed earlier by Stannett and Szwarc [57]. On the basis of a comparison of polymerisation rates and molecular weights of the polymers the following series of activities was found for the three lactones: ϵ-caprolactone > δ-valerolactone $\geqslant$ $\geqslant$ β-propiolactone, and from ϵ-caprolactone and δ-valerolactones polymers with $M \simeq 100\,000$ were obtained.

Satome and Hadira [58] effected the polymerisation of δ-valerolactone in the presence of ethyleneglycol and ethanolamine for 10 h at 100–180°C. Since the molecular weight of the polymers obtained did not exceed 2000 and the melting point was < 50°C, the course of the process was followed by the change in the refractive index n_D^{50} of the reaction mixture. The molecular weight of the polymer formed increased linearly with the ratio $[M]/[C]$; water in the system at a concentration < 0.01% had no significant effect on the rate of the process but catalytic additions of H_2SO_4, $AlCl_3$, or Na accelerated the reaction, their activity falling in the sequence H_2SO_4 > $AlCl_3$ > Na. The activation energy of the process was 6.4 kcal $mole^{-1}$. The suggested mechanism of initiation and growth of the polymeric chain is analogous to that proposed earlier [17]. On esterification of the synthesised polymer at the terminal OH groups a polyester thermostable at 200°C (it did not lose weight on heating at 200°C for 6 h) was obtained.

Several patents dealing with the polymerisation of ϵ-caprolactones in the presence of chelates of the Group IV metals of the Periodic System and of acylates of fatty acids[59]; a series of alkoxides of Sn, Pb, and Mn[60]; mineral acids and Lewis acids[61]; alcohols, amines, and amino-alcohols[62]; alkoxides of Na, K, Li; $LiAlH_4$; $NaBH_4$;[63] organometallic compounds of Periodic Group I, II, and III;[64,65] borates and oxides of Zn and Pb; and organotitanium compounds[66] have been published. The molecular weights of polymers described in the patents listed varied in a wide range from 900 to 250 000. These polymers are recommended to be used for obtaining fillers, coatings, lacquers, films, and fibres, and mixed with other polymers[67,68], for the preparation of various plastics.

IV. COPOLYMERISATION OF LACTONES

With the aim of increasing the thermal stability and of simultaneously retaining the valuable properties of lactone polymers, studies were undertaken on the copolymerisation of a series of lactones with vinyl or other cyclic monomers. The greatest number of papers deals with the copolymerisation of β-propiolactone and the second component most frequently used is a cyclic ether. The copolymerisation of β-propiolactone with 3,3-bischloromethyloxacyclobutane (BCCB)[69-67] in the presence of BF_3.ether and of the $Al(C_2H_5)_3-H_2O$ system at $-50°$ and 0°C has been described. On the basis of the elemental analysis and infrared spectra it has been found that both components react and form a copolymer, which consists of chloroform-soluble and chloroform-insoluble fractions, with m.p. ~ 125° and ~ 160°C respectively. BCCB is a more active monomer both in cationic and in anionic copolymerisation. Alkaline hydrolysis shows the block structure of this copolymer. Furukawa and coworkers[72] carried out the copolymerisation of β-propiolactone with tetrahydrofuran, epichlorohydrin, and ethylene oxide in the presence of the same catalysts at 0°C. Tetrahydrofuran and especially epichlorohydrin form with β-propiolactone in the presence of $Al(C_2H_5)_3-H_2O$ almost alternating copolymers. In using BF_3.ether copolymers are obtained only with tetrahydrofuran ($r_1 = 2.9$, $r_2 = 0.4$). Propylene oxide does not undergo copolymerisation with β-propiolactone.

An interesting attempt to obtain a copolymer of β-propiolactone with γ-butyrolactone was made by Furukawa and coworkers[73], who carried out the copolymerisation of these monomers in the presence of $Al(C_2H_5)_3-H_2O$, $Zn(C_2H_5)_2-H_2O$, $Al(iso\text{-}C_3H_7O)_3$, KOH, and K_2CO_3 at 0° and 25°C in the bulk and in solution (toluene, methylene chloride). The copolymer of β-propiolactone with γ-butyrolactone is formed only in the presence of the catalytic system $Al(C_2H_5)_3-H_2O$. From the constant activity of the monomers ($r_1 = 18 \pm 2$, $r_2 = 0.36 \pm 0.1$) it was concluded that γ-butyrolactone enters into the composition of the copolymer to an insignificant amount in the form of blocks with not more than two or three units of γ-butyrolactone.

The possibility of the copolymerisation of β-propiolactone with vinyl compounds was also studied. In the reaction[74] of acrylonitrile with β-propiolactone in the presence of such organometallic compounds as $SrZn(C_2H_5)_4$, $Al(C_2H_5)_3$, sodium naphthenate, and systems of C_4H_9Li with $Al(C_2H_5)_3$, $B(C_4H_9)_3$, $Cd(C_2H_5)_2$ at room temperature a mixture of chloroform-soluble and chloroform-insoluble products was formed. The soluble fraction consisted of a homopolymer of β-propiolactone and the insoluble contained a homopolymer of acrylonitrile and its copolymer with β-propiolactone. However, the yield of copolymer was insignificant and the rate of reaction low.

The grafting of β-propiolactone to the copolymer of acrylonitrile and diketen has been described[75]. The addition of β-propiolactone here proceeded owing to the opening of the diketen ring in the copolymer, that is, the diketen served as a transition link between the vinyl and the cyclic compound, uniting two types of polymerisation. Therefore a direct relation was observed between the diketen concentration in the copolymer of it with acrylonitrile and the quantity of graft β-propiolactone.

In the radical copolymerisation[76] of styrene with β-propiolactone in the ratio 85 : 15 a block copolymer with terminal OH and COOH groups is formed correspondingly. Block copolymers of styrene and β-propiolactone are also obtained in cationic copolymerisation ($SnCl_4$, 0°C, in toluene)[77].

In an attempt to obtain copolymers of β-propiolactone with propylene sulphide in the presence of $(C_2H_5)_3N$ and also with the *N*-carboxy-anhydride of DL-valine in the presence of pyridine it was found that in the first instance copolymerisation does not take place and in the second a compolymer with $M \simeq 1200$ is formed, with the copolymerisation constant showing low activity of the β-propiolactone[78].

The copolymerisation of β-propiolactone, γ-butyrolactone, and ϵ-caprolactone with ethyleneimine has been investigated[79]. The copolymerisation was carried out in the presence of $SnCl_4$, BF_3.ether, $(C_2H_5)_3N$, NaCN, and $HgCl_2$, in various solvents with dielectric constants from 2.38 to 37.6 at temperatures of $-35-0$°C, 35–100°C, and 100°C, for the β-, γ-, and ϵ-lactones respectively. Low-molecular-weight products were obtained. The yield of copolymers increases with increase in the dielectric constant of the solvent. On the basis of a comparison of the infrared spectra of the products synthesised and of model compounds containing the elementary unit of the polymer, five different structures were proposed according to the site of the opening of the lactone ring. Two structures are formed owing to the breaking of the Alk-O bond in the β-propiolactone in solvents with a high dielectric constant. In a medium with a low dielectric constant ring opening takes place at the acyl bond in all the lactones listed, independently of the medium.

Yamashita and coworkers described the copolymerisation of $\beta\beta$-dimethyl-β-propiolactone with 3,3-bischloromethyloxacyclobutane[52] and with styrene[77]. In addition, they investigated the copolymerisation of 3,3-bischloromethyloxacyclobutane with unsubstituted β-propiolactone, α-methyl-, β-methyl-, $\alpha\alpha$-dimethyl-, $\beta\beta$-dimethyl-, and β-isopropyl-β-propiolactone, which was carried out in the presence of BF_3.ether at 0°C. The greatest activity in cationic copolymerisation is exhibited by $\beta\beta$-dimethyl-β-propiolactone. It is thought that the mechanism of the ring opening of this monomer differs from the others because the two methyl groups at the β-carbon atom, owing to a redistribution of the electron density of the ring, facilitate breaking of the Alk–O bond with the formation of a tertiary carbonium ion. In the remaining investigations of lactones under the selected conditions ring opening takes place at the acyl–O bond. The following series of activities of these lactones in cationic copolymerisation with 3,3-bischloromethyloxacyclobutane was obtained: $\beta\beta$-dimethyl- $\gg$ $\gg$ β-methyl > unsubstituted $\geqslant$ α-methyl > $\alpha\alpha$-dimethyl. The activity of lactones in copolymerisation increases with increase in the number of alkyl substituents at the β-carbon atom, owing to an increase in the nucleophilic nature of the ester oxygen of the lactone ring. However, this value in β-lactones is low in comparison with simple cyclic esters, which is particularly clear on comparing the values

of the copolymerisation constants. Thus for the most active ββ-dimethyl-β-propiolactone $r = 1.42 \pm 0.1$ but for 3,3-bischloromethyloxacyclobutane $r = 7.24 \pm 0.32$. The reason for the comparatively low activity of β-lactones is thought to be the low nucleophilic nature of the ester oxygen owing to the drawing off of the electrons by the adjacent carbonyl group. A general tendency was noted for a decrease in the activity of β-lactones on the introduction of alkyl substituents in the α-position in anionic polymerisation and an increase in activity on the introduction of alkyl substituents in the β-position in cationic polymerisation, which is correspondingly reflected in the properties of the polymers.

Higher lactones, for example, γ-butyrolactone and ε-caprolactone give copolymers with ethyleneimine[79], as mentioned above, and also with 3,3-bischloromethyloxacyclobutane and β-propiolactone[80]. In the last instance the copolymerisation was carried out in the presence of BF_3.ether at room temperature or at 0°C. These lactones form copolymers with 3,3-bischloromethyloxacyclobutane, the activity in the copolymerisation of the lactones being in the following order: ε-caprolactone > γ-butyrolactone > > β-propiolactone. On the basis of the copolymerisation constants it was found that the activity of ε-caprolactone is higher than that of 3,3-bischloromethyloxacyclobutane but that of γ-butyrolactone is somewhat less. In the copolymerisation of β-propiolactone products of comparatively low molecular weight ($[\eta] = 0.06-0.25$) are obtained.

On the basis of the studies reviewed it can be concluded that lactones are of interest both for studying polymerisation processes connected with ring-opening and as prospective raw materials for obtaining polyesters which exhibit several valuable properties.

REFERENCES

1. F. Fichter and A. Beisswenger, Ber., 36, 1200 (1903).
2. E. Hollo, Ber., 61, 895 (1928).
3. F. J. van Natta, G. L. Dorough, and W. H. Carothers, J. Amer. Chem. Soc., 54, 761 (1932).
4. T. L. Gresham, J. E. Jansen, F. W. Shaver, and J. T. Gregory, J. Amer. Chem. Soc., 70, 999 (1948).
5. T. L. Gresham, J. E. Jansen, F. W. Shaver, and J. T. Gregory, J. Amer. Chem. Soc., 70, 1001 (1948).
6. T. L. Gresham, J. E. Jansen, F. W. Shaver, and J. T. Gregory, J. Amer. Chem. Soc., 70, 1003 (1948).
7. T. L. Gresham, J. E. Jansen, F. W. Shaver, and J. T. Gregory, J. Amer. Chem. Soc., 70, 1005 (1948).
8. T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bannkert, W. L. Bareet, and M. G. Brandergard, J. Amer. Chem. Soc., 71, 661 (1949).
9. T. L. Gresham, J. E. Jansen, F. W. Shaver, and R. A. Bannkert, J. Amer. Chem. Soc., 71, 2807 (1949).
10. T. L. Gresham, J. E. Jansen, and F. W. Shaver, J. Amer. Chem. Soc., 72, 72 (1950).
11. T. L. Gresham, J. E. Jansen, F. W. Shaver, M. R. Friderick, and W. L. Bareet, J. Amer. Chem. Soc., 73, 2345 (1951).
12. T. L. Gresham, J. E. Jansen, F. W. Shaver, and F. T. Fiedorek, J. Amer. Chem. Soc., 74, 1323 (1952).
13. T. L. Gresham, J. E. Jansen, and F. X. Werber, J. Amer. Chem. Soc., 76, 609 (1954).
14. Belg. P. 662 526 (1951); Chem. Abs., 47, 3872f (1953).
15. S. C. Westfahl and T. L. Gresham, J. Org. Chem., 21, 1145 (1956).
16. T. L. Gresham, J. E. Jansen, and F. W. Shaver, J. Amer. Chem. Soc., 70, 998 (1948).
17. H. Cherdron, H. Ohse, and F. Korte, Makromol. Chem., 56, 179 (1962).
18. M. Okada, Y. Yamashita, Y. Ichikawa, T. Tsuda, and S. Miura, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 104 (1963).
19. Y. Yamashita, Y. Ishikawa, and T. Tsuda, J. Chem. Soc. Japan, Ind. Chem. Sect., 67, 252 (1964).
20. Jap. P. 15 244 (1961); Ref. Zhur. Khim., S267 (1965).
21. Jap. P. 15 245 (1961); Ref. Zhur. Khim., S268 (1965).
22. T. Kagiya, T. Sano, and K. Fukui, J. Chem. Soc. Japan, Ind. Chem. Sect., 67, 951 (1964).
23. S. Inove, I. Tomoi, T. Tsuruta, and J. Furukawa, Makromol. Chem., 48, 229 (1961).
24. J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawasaki, and T. Tatano, J. Chem. Soc. Japan, Ind. Chem. Sect., 65, 254 (1962).
25. H. Cherdron, H. Ohse, anf F. Korte, Makromol. Chem., 56, 187 (1962).
26. Y. Yamashita, T. Tsuda, Y. Ishikawa, and S. Miure, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 109 (1963).
27. T. Kagiya, T. Sano, and K. Fukui, J. Chem. Soc. Japan, Ind. Chem. Sect., 68, 1144 (1965).
28. S. Okamura, T. Hagishimura, and A. Tanako, J. Chem. Soc. Japan, Ind. Chem. Sect., 65, 707 (1962).
29. T. Kagiya, T. Sano, and K. Fukui, J. Chem. Soc. Japan, Ind. Chem. Sect., 68, 1141 (1965).
30. Y. Etienne and R. Soulas, J. Polymer Sci., C4, 1061 (1963).
31. R. Tsuzuki, K. Ichikawa, and M. Kase, J. Org. Chem., 26, 1808 (1961).
32. U. S. P. 2 719 156 (1955); Chem. Abs., 13100a (1956).
33. U. S. P. 2 744 130 (1956); Chem. Abs., 17531 (1956).
34. Jap. P. 6394 (1963); Ref. Zhur. Khim., S178 (1965).
35. Jap. P. 6394 (1963); Ref. Zhur. Khim., S179 (1965).
36. G. C. Daul, R. M. Reinhart, and I. D. Reid, Textile Res. J., 25, 330 (1955).
37. W. C. Rose and H. P. Lundgren, Textile Res. J., 23, 930 (1953)
38. Jap. P. 6391 (1961); Ref. Zhur. Khim., S288 (1966).
39. S. Okamura and K. Hayashi, J. Chim. phys., 59, 429 (1962).
40. S. Okamura, K. Hagishimura, and Y. Kianishi, J. Polymer Sci., 58, 925 (1962).
41. K. Hayashi, S. Mori, I. Nakai, and S. Okamura, Makromol. Chem., 68, 194 (1963).
42. Jap. P. 13 895 (1962); Ref. Zhur. Khim., S193 (1965).
43. C. David, J. Parren, F. van der Provoost, and A. Ligotti, Polymer, 3, 341 (1963).
44. M. Sakamoto, K. Hayashi, and S. Okamura, J. Polymer Sci., B3, 205 (1965).
45. Jap. P. 6392 (1961); Ref. Zhur. Khim., S289 (1966).
46. U. S. P. 3 111 469 (1963); Ref. Zhur. Khim., 196 (1965).
47. S. Okamura, T. Hagishimura, A. Tanako, R. Kato, and Y. Hikuoshi, Makromol. Chem., 54, 226 (1962).
48. G. Wasai, T. Saegusa, and J. Furukawa, J. Chem. Soc. Japan, Ind. Chem. Sect., 67, 601 (1964).
49. D. Gianalvise, Chim. Ind. (Milan), 46, 525 (1964).
50. French P. 1 231 163 (1960); Chem. Abs., 55, 19330f (1961).
51. R. Thiebout, N. Fischer, Y. Etienne, and I. Coste, Ind. Plastiques Mod. (Paris), 2, 1 (1962).
52. Y. Yamashita, T. Tsuda, Y. Ishikawa, and T. Shimizu, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 1493 (1963).
53. K. Fukui, H. Kato, T. Ionezawa, and S. Okamura, Bull. Chem. Soc. Japan, 37, 904 (1964).
54. Canad. P. 549 347 (1957); cited by W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 298.
55. T. D. D'yachenko, N. A. Glukhov, M. M. Koton, and Yu. N. Sazanov, in Collected Papers, "Vysokomolekularnye Soedinenie. Geterotsepnye Vysokomolekularnye Soedineniya" (High-Molecular-Weight Compounds. Hetero-chain High-Molecular-Weight Compounds), Izd. Akad. Nauk SSSR, Moscow, 1964, p. 236.

56. Yu.N.Sazanov, M.M.Koton, N.A.Glukhov, and T.D.D'yachenko, Paper presented at the XVth All-Union Conference on High-Molecular Weight Compounds, Moscow, 1965.
57. V.Stannett and M.Szwarc, J.Polymer Sci., 10, 587 (1954).
58. K.Satome and Y.Hadira, Makromol.Chem., 82, 41 (1965).
59. U.S.P. 2 878 236 (1959); Chem.Abs., 53, 12744a (1959).
60. U.S.P. 2 890 208 (1959); Chem.Abs., 53, 18546h (1959).
61. U,S.P. 2 914 556 (1959); Chem.Abs., 54, 8586d (1960).
62. B.P. 859 645 (1961); Chem.Abs., 56, 20505g (1961).
63. B.P. 981 199 (1965); Ref.Zhur.Khim., S217 (1966).
64. B.P. 859 642 (1961); Chem.Abs., 56, 25355g (1961).
65. B.P. 1 000 401 (1965); Ref.Zhur.Khim., S.280 (1966).
66. U.S.P. 3 164 945 (1965); Ref.Zhur.Khim., S285 (1966).
67. U.S.P. 2 933 477 (1960); Chem.Abs., 54, 21830c (1960).
68. U.S.P. 2 933 478 (1960); Chem.Abs., 54, 21830e (1960).
69. K.Tada, T.Saegusa, and J.Furukawa, J.Chem.Soc.Japan, Ind.Chem.Sect., 66, 996 (1963).
70. K.Tada, T.Saegusa, and J.Furukawa, Makromol.Chem., 71, 71 (1964).
71. T.Shimizu, T.Tsuda, and Y.Yamashita, J.Chem.Soc.Japan, Ind.Chem.Sect., 67, 1661 (1964).
72. K.Tada, T.Saegusa, and J.Furukawa, J.Chem.Soc.Japan, Ind.Chem.Sect., 66, 1501 (1963).
73. K.Tada, Y.Numata, T.Saegusa, and J.Furukawa, Makromol.Chem., 77, 220 (1964).
74. Y.Shimosaka, T.Tsuruta, and J.Furukawa, J.Chem.Soc.Japan, Ind.Chem.Sect., 66, 1498 (1963).
75. T.Shiota, Y.Hiraki, Y.Goto, K.Hayashi, and S.Okamura, J.High Polymer (Tokyo), 22, 252 (1965).
76. U.S.P. 2 895 658 (1958); Chem.Abs., 53, 15642f (1959).
77. T.Tsuda, T.Shimizu, and Y.Yamashita, J.Chem.Soc.Japan, Ind.Chem.Sect., 67, 2145 (1964).
78. O.C.Dermer and W.A.Ames, J.Polymer Sci., A-2, 9, 4151 (1964).
79. T.Kagiya, S.Narisawa, K.Manabe, and K.Fukui, J.Chem.Soc.Japan, Ind.Chem.Sect., 68, 1741 (1965).
80. T.Tsuda, T.Shimizu, and Y.Yamashita, J.Chem.Soc.Japan, Ind.Chem.Sect., 67, 2150 (1964).

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad

U. D. C. 541.183.27 : 542.934.1

Gas Hydrates

S.Sh.Byk and V.I.Fomina

This review states contemporary views about gas hydrates, and also about non-stoichiometric clathrates with the general formula $M.nH_2O$. The known types of the hydrates and their crystal structure are described. The thermodynamics of hydrate formation is considered. Methods of determining the composition of the hydrates are described. Factual information concerning the hydrates of individual gases and organic liquids and mixed hydrates (binary and multicomponent) is given. The problem of the stabilisation of hydrates by an auxiliary gas is considered. Information is given about the density of hydrate crystals and the physical kinetics of the hydrate formation. Equations are given which are obtained by the methods of statistical mechanics and are based on the use of Lennard-Jones and Kihara potentials, and allow the main thermodynamic properties of the hydrates to be calculated. The problems of the industrial utilisation of the hydrates are examined (desalination of sea water, separation of liquid and gaseous mixtures, etc.). The theoretical principles of the inhibition of hydrate formation processes are stated. Bibliography of 180 references.

CONTENTS

I. Introduction 469
II. Contemporary views about gas hydrates 470
III. Conditions for the formation of hydrates 471
IV. Methods of preparation and of determining the composition of hydrates 472
V. Thermodynamics of hydrate formation 473
VI. Stabilisation of hydrates with the aid of an "auxiliary gas" 474
VII. Hydrates of individual gases and volatile organic liquids 474
VIII. Mixed hydrates 480
IX. Calculation of the conditions of hydrate formation and of the compositions of the solid (hydrate) and gas phases 484
X. Use of the principles of statistical mechanics in studying gas hydrates. 486
XI. Physical kinetics of the formation of hydrates. 487
XII. Density of hydrate crystals 487
XIII. Industrial use of gas hydrates 488
XIV. Prevention of hydrate formation 488

I. INTRODUCTION

Gas hydrates are solid crystalline substances with the appearance of snow or loose ice and the general formula $M.nH_2O$, where M is the hydrate-forming molecule. There is considerable theoretical interest in the investigation of gas hydrates, as they allow general laws to be formulated which describe the unique physical properties of an extensive group of clathrate compounds† in which the crystal

† Contemporary views about gas hydrates as non-stoichiometric clathrates are presented in Chapter II of this review.