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SOME REGULARITIES IN THE POLYMERISATION OF BIFUNCTIONAL MONOMERS

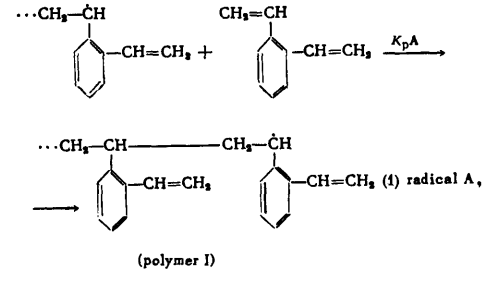
V. V. Amerik and B. A. Krentsel'

The development of processes of linear and stereospecific polymerisation, which has considerably extended the range of polymerisable compounds and opened up new possibilities for controlling the growth of macromolecules, has given rise to a natural interest in the polymerisation of bifunctional monomers. Several new regularities have been discovered in the polymerisation of these monomers, which are of scientific and practical importance.

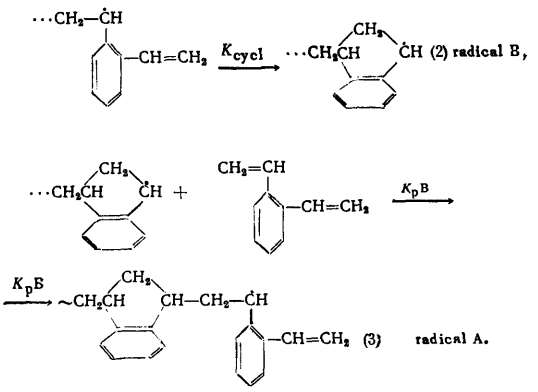
In the polymerisation of the simplest symmetrical bifunctional monomer, butadiene, either 1,2- or 1,4-addition is possible. A polymer chain of desired structure can be obtained by using a definite type of catalyst. The polymerisation of bifunctional compounds in which the two carbon–carbon double bonds differ in electron density is still more influenced by the type of catalyst (cationic or anionic) and by the solvent.

If a bifunctional compound containing a heteroatom attached to one of the double bonds is used as monomer, the structure of the resulting polymer depends not only on the nature of the catalyst and the solvent but also on the temperature of polymerisation. In spite of several investigations published in the literature, these questions are still far from being completely elucidated.

The polymerisation of bifunctional compounds containing two double bonds in the *ortho*-position has been studied with *o*-divinylbenzene as example [1]. This monomer was polymerised by a radical mechanism (with $\alpha\alpha'$-azoisobutyronitrile as initiator) in benzene solution. The resulting soluble polymer still contained double bonds, as was confirmed by their spectra and by bromination in carbon tetrachloride. Therefore the following three reactions can be assumed for growth of the polymer chain:



(polymer I)



The mole fraction of monomer units containing unchanged vinyl groups is given by the equation

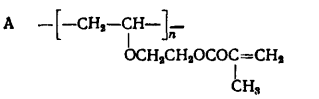
$$-\frac{dm}{dM}=\frac{2[M]}{2[M]+r_c}\quad r_c=\frac{K_{cycl}}{K_pA},$$

where [M] is the molar concentration of monomer and m the concentration of polymer (I). It is obvious from this equation that the content of monomer units containing unchanged vinyl groups will depend on the initial concentration of the monomer, since r_c is constant.

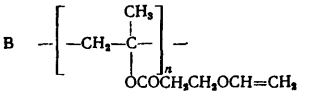
If the polymer contains one vinyl group per monomer unit, the content of polymer (I) is taken as 100%. Usually, however, it was always less than 100%, varying from 30% to 90% depending on the conditions of polymerisation. The content of monomer units containing vinyl groups falls with a decrease in the concentration of monomer in the initial mixture and with a rise in the temperature of polymerisation, since conditions favouring the cyclisation reaction (2) are produced. This fact is explained by the difference in activation energy between the bimolecular growth in the polymer chain (1) and the intramolecular cyclisation (2). Addition of *o*-divinylbenzene in the growth reaction occurs in the same way as with styrene. The growing radical A has a rather larger delocalisation energy than the styrene radical, while the cyclic radical B possesses a far smaller delocalisation energy. Hence a higher activation energy is required for intramolecular cyclisation than for addition of the monomer. The thermal polymerisation of *o*-divinylbenzene therefore results in formation of a linear polymer containing five-membered rings. Chain growth takes place mainly in conformity with Eqn. (1).

Various bifunctional monomers containing two or more carbon–carbon double bonds have been synthesised[2], and found to differ greatly in their tendency to form growing ions or free radicals depending on the mode of initiation of the reaction. Vinyl ethers of phenols containing the unsaturated side-chain $CH_2:CHOCH_2CH_2OR$, where R represents phenyl, allylphenyl, methylallylphenyl, 2-allyl-4-chlorophenyl, or but-2-enyl, were subjected to low-temperature polymerisation in the presence of boron trifluoride. Linear polymers were obtained, whose infrared spectra confirmed that the vinyloxy-group was involved in the polymerisation. This is explained by the greater electron density on the vinyloxy-bond and the greater reactivity of the latter compared with the allyl functional group.

The unsuccessful attempt to polymerise the resulting oligomers at the allyl double bond by using radical initiators is explained by the so-called degradation mechanism of chain transfer[3]. The radical which is formed is strongly stabilised by delocalisation of the unpaired electron. Polymerisation of 2-vinyloxyethyl methacrylate with cationic and anionic catalysts gave polymers of varying structures. This compound $CH_2:C(CH_3)COOCH_2CH_2OCH:CH_2$ contains two types of double bonds, the electron-rich vinyloxy-bond and the electron-deficient methacrylate double bond[4]. Chain growth takes place differently with cationic and with anionic catalysts, giving polymers of structures A and B respectively



(cationic catalyst),

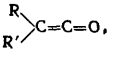


(anionic catalyst).

The polymerisation of 2-vinyloxyethyl methacrylate over tin(IV) chloride has been described[5]. The infrared spectra of the polymer obtained by polymerisation in solution in carbon tetrachloride at 0° showed complete disappearance of the 1780 cm^{-1} band characteristic of the vinyloxy-group, while the bands at 1000–1650 cm^{-1} characteristic of the methacrylate double bond remained. Consequently the resulting polymer had structure A. Polymerisation of 2-vinyloxyethyl methacrylate on a Ziegler catalyst at -20° gave a polymer of structure B, soluble in benzene. Polymerisation on the same catalyst at +25° gives a mixture of A and B polymers (see Table 1).

It can be assumed from these results that the nature of the active centres in Ziegler catalysts depends not only on the proportions of the components but also on the temperature of polymerisation. This is probably the reason for the contradictory results obtained by many authors in attempting to classify these catalysts as anionic or cationic.

A no less interesting class of bifunctional compounds are those in which a carbon–carbon double bond is accompanied by a carbonyl double bond. Among such monomers are keten, dimethylketen, biketen, and acrylaldehyde. The presence of cumulative carbon–carbon and carbonyl double bonds in ketens

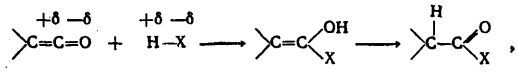


makes them highly reactive towards polar and non-polar molecules. The latter add on at the carbon–carbon double bond, and polar molecules at the carbonyl double bond. In many reactions, however, the products of addition to the

TABLE 1. Polymerisation of 2-vinyloxyethyl methacrylate on various catalysts.

Catalyst	Solvent	Temp., °C	Conversion, %
$SnCl_4$	CCl_4	−20	90A
$TiCl_4$ + Al(iso-C_4H_9)$_3$	C_6H_{12}	−20	13B
Al/Ti 1.2 : 1			
$TiCl_4$ + Al(iso-C_4H_9)$_3$	C_6H_{12}	+25	12A
Al/Ti 1.2 : 1			2B
Li tri-n-butylamine	$(C_4H_9)_3N$	−25	30B
Triethylboron	C_6H_6	25	12A

carbonyl group, which are in the enolic form, pass into carbonyl compounds:

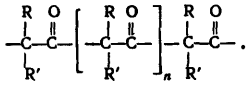


where HX is a substance containing polar groups.

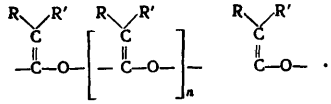
Structural units retaining the original form can therefore be observed only when keto–enol rearrangement in the reaction products is impossible, i.e. in the polymerisation of ketens. Linear and regular polymers of ketens may contain two structural units



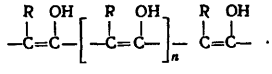
Regular "head-to-tail" addition of α-monomer units gives macromolecules having an α-ketonic structure



Similar addition of β-monomer units gives a polyacetal structure

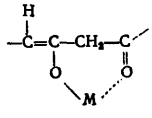


If R and R′ are hydrogen atoms, the α-ketonic structure is in equilibrium with the enolic structure



In most cases only products of low molecular weight were isolated in the polymerisation of keten (see Table 2).

Natta and his coworkers[9] have attempted to polymerise keten using Friedel–Crafts catalysts ($ZnCl_2$, $AlCl_3$) and organometallic catalysts (triethylaluminium and butyllithium, di-n-butylzinc), and have obtained compounds having a chelate type of structure

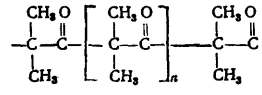


where M represents the metal. Degrees of conversion were low owing to deactivation of the catalyst.

Chelate structures are not formed if hydrogen atoms are not present in the monomer. At an early date Staudinger observed[7,10] the polymerisation of dimethylketen in the presence of trimethylamine as catalyst at -80°. The polymer had no regular chemical structure, and was completely converted into the monomer over the temperature range 100–200°.

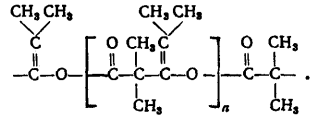
Polymers of dimethylketen having a regular structure have been obtained[9,11] with several types of catalysts — (1) acidic catalysts, which in most cases act by a cationic mechanism, and have the formula AlX_nR_{3-n}, where X is a halogen, R is an alkyl or an aryl radical, and n = 1–3; and (2) catalysts of anionic type, containing metals of small ionic radius and possessing electronegativities not exceeding 1.6, such as triethylaluminium, diethylberyllium, ethyllithium, etc. (see Table 3).

With the first group of catalysts dimethylketen yields a white polymer of 60–80% crystallinity. The polymer is soluble only in strongly polar solvents of high boiling point. It melts close to 250°, and is thermally stable up to 300°, within which temperature limits it is not depolymerised to the monomer. Intense absorption bands in the region of 5.9 μm in the infrared spectra, and in the region of 259 mμm in the ultraviolet spectra, indicate the presence of carbonyl groups in the polymer, which suggests an α-ketonic structure



(I)

The dimethylketen polymer (II), obtained in the presence of catalysts of the second group, differs markedly in structure from polymer (I). Its infrared and ultraviolet spectra confirm its polyester structure, since the absorption band due to carbonyl groups is weak, while a band is observed in the region of 5.74 μm, which is characteristic of ester groups



(II)

The structures of polymers (I) and (II) are confirmed also by chemical methods.

TABLE 2. Products of the polymerisation of keten.

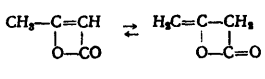
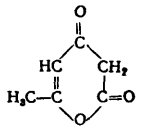
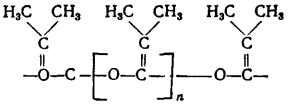
Conditions of polymerisation	Products obtained	Ref.
0–50°, no catalyst		6
70–120°, pyridine as catalyst		7
-78° in acetone solution	$(C_2H_2O)_4$	8

TABLE 3. Polymerisation of dimethylketen in the presence of various catalysts at -78°.

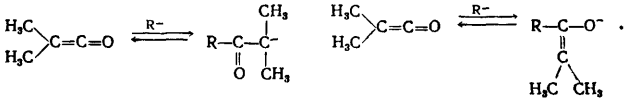
Catalyst	Solvent	Conversion, %	Time, min	Structure of polymer		
				polyketone	polyester	polyacetal
$AlBr_3^*(C_2H_5)_2O$	toluene	18	360	+		
$AlBr_3$	ether	22	1800	+		
Na–naphthalene	toluene	32	1440		+	
Na–naphthalene	dimethylformamide	55	1440			+
C_2H_5ONa	toluene	100	10			+
Na–naphthalene	toluene	93	3			+
C_4H_9Li	tetrahydrofuran	86	12			+
C_4H_9Li	toluene	18	1440		+	
$Al(C_2H_5)_3$	toluene	8	1440		+	
$BrMgC_6H_5$	toluene	15	1440	+	+	
$Zn(C_2H_5)_2$	–	10	1440		+	
$(C_2H_5)_2NH$	toluene	35	1440		+	+

* Polymerisation carried out at -50°.

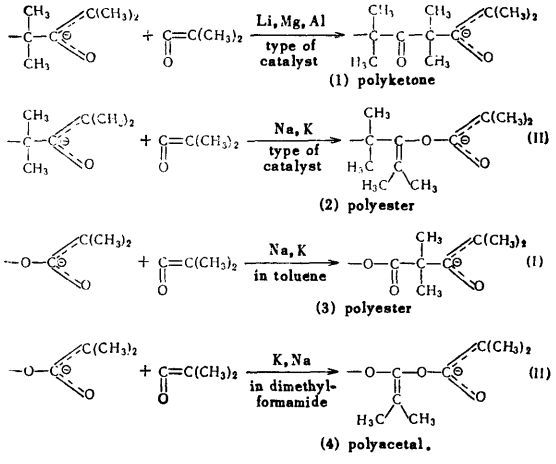
Polymers of dimethylketen which have a predominantly polyacetal structure have been obtained [11,12] by polymerisation in the presence of anionic catalysts (C_4H_9Li, C_4H_9OLi, Na–naphthalene, C_2H_5ONa). The polarity of the solvent influences the structure of the polymer obtained [12]. When dimethylketen is polymerised in the presence of the sodium–naphthalene complex as catalyst in toluene solution, polymers of polyester structure are obtained. Replacement of toluene (dielectric constant $\epsilon = 2.379$) by dimethylformamide (35.0) results in formation of a polymer of polyacetal structure. The infrared spectra of these polymers exhibit a band characteristic of carbon–carbon double bonds, and the products of acid alcoholysis and of hydrogenolysis in the presence of lithium tetrahydroaluminate indicate the presence of acetal links



The various reactions in the polymerisation of dimethylketen can be explained by postulating the following scheme for initiation and growth of the polymer chain [11,13,14]

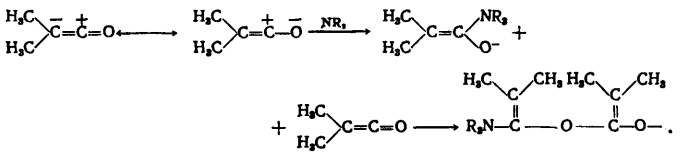


The following four types of reaction can be postulated in the stage of chain growth

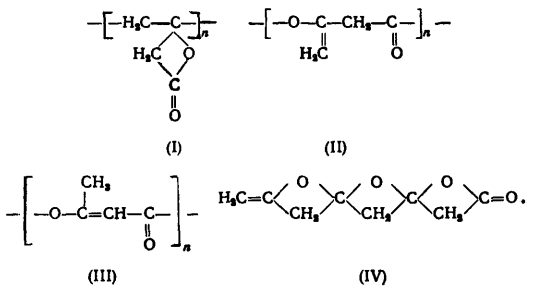


The driving force in the reaction of ketens with nucleophilic reagents is electrostatic interaction of the polarised keten molecule with electron-rich centres [15]. The anion (1) usually reacts with the next molecule of dimethylketen through the more electronegative oxygen atom according to Eqn. (2). The ester ion (II), under the influence of the oxygen atom, reacts more readily with the next monomeric molecule through the carbanion structure according to Eqn. (3). Polymerisation is also possible at the same time according to Eqns. (2) and (3) in the presence of catalysts containing sodium and potassium ions in toluene solution, which results in the formation of polyesters. Polyacetals are obtained, according to Eqn. (4), predominantly in polar solvents, such as dimethylformamide and triethylamine, which stabilise the enolic structure (II) by solvation. Japanese authors [14] give data on the polymerisation of dimethylketen in the presence of tertiary aliphatic amines. A more detailed study has shown [16] that the catalytic activity of tertiary amines increases with their dissociation constant. Increase in the polarity of the solvent results in an increased content of polyacetal structure in the polymer (see Table 4).

Polymerisation of dimethylketen in toluene also yields a considerable quantity of polyacetal structure, which represents an exception to the general rule of the effect of solvent polarity on polymer structure. It is interesting that, in dimethylformamide solution, dimethylketen polymerises in the absence of a catalyst. Dimethylformamide is probably sufficiently basic to initiate the polymerisation of dimethylketen in the absence of any other catalyst. In any case, rise in temperature results in a decrease in the proportion of polyacetal structure in the resulting polymer. The suggested mechanism of polymerisation when a series of amines are used as catalysts is that the first stage involves nucleophilic attack by the bases on the carbonyl group:



The influence of conditions on the polymerisation of biketen and the structure of the resulting polymer has been studied in less detail. The following four polymer structures can be imagined [17,18]



At room temperature biketen yields a dimer.

Fairly recently [19] a polymer of biketen of molecular weight ~ 1630 has been obtained in the presence of mercuric chloride as catalyst. It has the polyester structure (II).

TABLE 4. Effect of nature of solvent on polymerisation of dimethylketen at -40°; 50 ml of solvent, 0.4 vol. % of $(C_2H_5)_3N$.

Solvent	Dimethylketen, ml	Time of reaction, min	Yield of polymer, %	$\frac{D_{5.85\,\mu m}^{*}}{D_{5.66\,\mu m}}$
Cyclohexanone	10	30	70	4.7
Acetone	10	15	65	11.7
Diethyl ketone	10	15	65	9.0
Acetonitrile	10	15	83	6.3
Diethyl ether	10	15	4	(a)
Dimethylformamide (b)	10	15	100	5.3

* $D_{5.85\,\mu m}$ = intensity of absorption band characteristic of polyacetal structure;

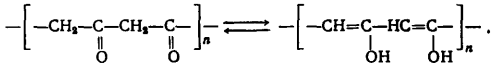
$D_{5.66\,\mu m}$ = intensity of absorption band characteristic of isolated polyester links.

(a) Mixture of polyester and polyacetal structures obtained.

(b) No catalyst present.

A polymer of polyester structure is also obtained[20] from biketen in the presence of aluminium ethoxide.

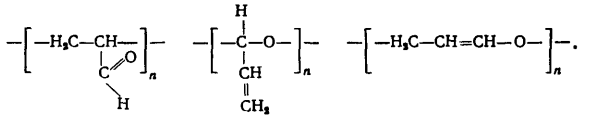
In the presence of boron trifluoride an amorphous polymer has been obtained[21,22] whose structure differs from those suggested previously. The molecular weight is comparatively low (2080) and the infrared spectra support a β-diketone structure



In ethylene glycol solution the ketonic form of the polymer is in equilibrium with the enolic form. This structure is confirmed also by the product obtained on reaction with phenylhydrazine, whose infrared spectrum has a band in the range 1600–1500 cm^{-1}, which is characteristic of the –C=C–C=N– grouping.

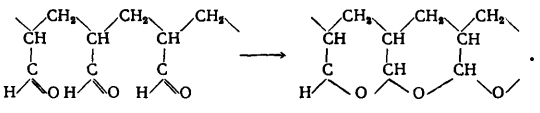
It is difficult to polymerise keten under these conditions, but the use of benzonitrile as catalyst has enabled a polymer of β-diketone structure to be obtained[22].

In the acrylaldehyde molecule, in contrast to dimethylketen, the two double bonds, carbon–carbon and carbon–oxygen, are conjugated. In the Diels–Alder reaction, acrylaldehyde acts as a diene[23,24], which suggests the formation of polymers having the structures



Several workers[25–27] have investigated the polymerisation of acrylaldehyde and studied the properties of the resulting polymers. Cationic polymerisation in the presence of aluminium chloride, zinc chloride, and ether complexes of boron trifluoride in various solvents (at 0–30°) yields soluble polymers containing reactive aldehyde groups (15–20%).

Koton and his coworkers have investigated[28] the polymerisation of acrylaldehyde in the presence of gaseous boron trifluoride with various additives over the range 0–80°. They obtained a vitreous polymer containing no free aldehyde groups. It is evident that the aldehyde group plays an active part in the polymerisation. The polymer is insoluble in organic solvents, but dissolves readily in sulphuric acid. Polymerisation takes place by a "head-to-tail" mechanism, all the aldehyde groups being located on the same side of the chain, which favours cyclisation through the $-C\overset{O}{\underset{H}{<}}$ group:



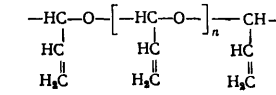
The cyclic structure of the polymer is indicated by its high thermal stability, while the absence of cross-linked structures is confirmed by the sharp melting point. Cyclisation does not occur on polymerisation on dilute solution.

Acrylaldehyde undergoes polymerisation in the 1,4-position in the presence of metallic sodium in boiling benzene[29]. The resulting polymer contains 5 mole % of aldehyde groups and 10–15% of double bonds.

Infrared and nuclear magnetic resonance data confirm that the polymer has the structure

$$[CH_2-CH=CH-O-CH_2-CH=CH-O]_n.$$

Anionic polymerisation of acrylaldehyde in the presence of various catalysts (see Table 5) between +25° and -78° yields polymers in whose infrared spectra the absorption band due to the carbonyl group (5.85 μm) has been considerably weakened or is completely absent[30]. The quantity of –C=C– double bonds, determined by hydrogenation of a solution of the polymer in glacial acetic acid, is 50–70%. Aldehyde groups were identified in the polymer by treating it with phenylhydrazine and then determining the nitrogen content. The proportion of aldehyde groups in polyacrylaldehyde obtained in the presence of anionic catalysts varies from 1% to 9%. The nature of the solvent affects not only the rate of polymerisation but also the chemical structure of the product. A decrease in the temperature of polymerisation and an increase in the polarity of the solvent decreases the quantity of free carbonyl groups in the polymer, which has the polyacetal structure



The epoxypropionaldehyde molecule, like that of acrylaldehyde, contains a reactive carbonyl group, but the position of the vinyl group is occupied by a heterocyclic ring, which can be regarded as a functional group. This aldehyde polymerises readily under the influence of catalysts of various types[20]. Thus triethylaluminium at -78° yields a polymer of polyacetal structure

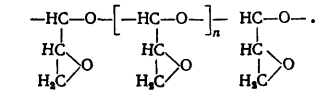
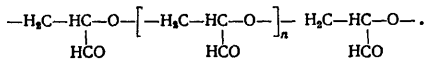


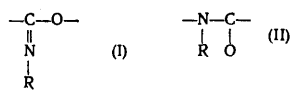
TABLE 5. Polymerisation of acrylaldehyde.

Solvent	ml	Acrylaldehyde, ml	Catalyst	mole %	Time, min	Temp., °C	Yield of polymer, %
Petroleum ether	25	5	n-C_4H_9Li	0.5	300	-20 to 30	–
Toluene	25	5	n-C_4H_9Li	1.0	780	-20 to -30	16
Toluene	30	5	n-C_4H_9Li	1.0	600	room temp.	91
Toluene	25	5	C_6H_5MgBr	4.5	60	room temp.	trace
Diethyl ether	30	5	$(C_6H_5)_3CNa$	0.5	180	-20	36
Diethyl ether	25	5	CH_3ONa	1.0	240	-30	46
Dimethoxymethane	45	5	K–benzophenone	0.5	150	-30	33
Tetrahydrofuran	25	5	Na–naphthalene	0.5	840	-78	5
»	45	5	Na–naphthalene	0.5	285	-50	79
»	145	5	Na–naphthalene	1.0	240	-50 to 60	66
»	50	5	K–benzophenone	0.5	150	-50 to 60	55
»	30	5	$(C_6H_5)_3CNa$	1.0	180	-30 to -40	93
»	25	5	CH_3ONa	1.0	150	-40	–
»	25	5	sodamide	1.0	180	-40	54
»	45	5	Na	1.0	225	-50	48
»	15	5	piperidine	1.0	105	0	40
»	20	5	C_4H_9MgBr	2.0	480	room temp.	trace
1,2-Dimethoxyethane	20	5	Na–naphthalene	1.0	120	-40	86
Acetonitrile	40	5	CH_3ONa	1.0	25	-35	48
Methyl acetate	30	5	CH_3ONa	1.0	120	-40 to 50	65
No solvent	–	15	n-C_4H_9MgBr	5.0	1440	room temp.	30

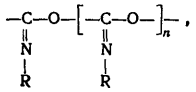
With aluminium isopropoxide, however, a polymer of polyepoxide structure is obtained



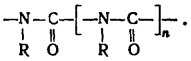
Isocyanates give dimers and trimers [31] in the presence of bases, triethylamine and pyridine. Two fundamental polymer structures



are possible on the stereospecific polymerisation of isocyanates. Regular opening of the carbonyl double bond gives a macromolecule of polyacetal structure

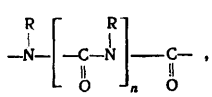


whereas regular opening of the carbon–nitrogen double bond yields an amide structure



Natta and others have obtained polymers of phenyl and butyl isocyanates by low-temperature polymerisation [32,33]. Only traces of polymers were formed in the presence of catalysts of cationic type, but with the corresponding anionic catalysts crystalline polymers of these isocyanates were formed (see Table 6).

The presence in the infrared spectra of an intense band characteristic of disubstituted amides suggests that the polymer has a polyamide structure



where R represents phenyl or butyl. Polymers having the polyacetal or mixed structure were not obtained.

Analysis of the above results on the polymerisation of bifunctional monomers enables the following general conclusions to be drawn:

1. In the polymerisation of a bifunctional compound containing double bonds differing in electron density, the structure of the resulting polymer is determined to a considerable extent by the choice of catalyst (anionic or cationic).

TABLE 6. Polymerisation of phenyl and n-butyl isocyanates.

Isocyanate	Catalyst	Solvent	Temperature, °C	Conversion, %
Phenyl	$AlBr_3$ in heptane	toluene	−60	trace
Butyl		toluene	−78	–
Phenyl	C_2H_5Li in benzene	CS_2	−78	34.5
Butyl		CS_2	−78	76.0
Phenyl		toluene	−78	45
Butyl	C_2H_5Li	toluene	−78	43

2. Growth of the polymer chain is determined not only by the reactivity of each bond but also by the polar effect. In the polymerisation of dimethylketen, for example, a polyester structure is formed: i.e. there is a strongly marked tendency for alternating polymerisation at the carbon–carbon and the carbonyl double bond. This results in formation of a characteristic copolymer.

3. Decrease in the temperature of polymerisation of monomers containing carbon–carbon and carbonyl double bonds results in increased specific gravity in the polymer of polyacetal structure. The structure of the polymer is probably determined by the thermodynamics of the process. At lower temperatures polymerisation becomes possible with a small heat of reaction: i.e. a polymer of mixed and polyacetal structure can be formed.

4. The polarity of the solvent affects not only the rate of polymerisation but also the structure of the polymer chain. An extreme case is provided by dimethylformamide, in which dimethylketen polymerises in the absence of a catalyst.

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U.D.C. 541.6 : 547.313.2

THE FREE-RADICAL COPOLYMERISATION OF ETHYLENE

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I. INTRODUCTION

Copolymerisation has now acquired considerable importance as a method which makes it possible to alter the properties of a polymer in a required direction. By selecting different combinations of ethylene with appropriate monomers, it is possible to vary over a wide range such properties of the polymer as its strength, elasticity, melting point, adhesive properties, solubility, etc.[1,2] Copolymers of ethylene can be prepared both by free-radical copolymerisation and by ionic copolymerisation. The free-radical process, in particular, is of considerable interest, since in this case the number of monomers which can be used with ethylene is much greater than for ionic copolymerisation. The ionic process is carried out chiefly with monoalkene and diene hydrocarbons, whereas the copolymerisation of ethylene by the free-radical mechanism can be carried out not only with these hydrocarbons but also with a large number of compounds of different types, including halogenated alkenes, vinyl esters and ethers, acrylic monomers, and even compounds which do not polymerise independently, such as sulphur dioxide and carbon monoxide[1,2]. Moreover, the presence of different functional groups (e.g. acetate and carbonyl groups) in the copolymers prepared by radical copolymerisation makes it possible to convert these polymers, by means of chemical reactions, into a number of new copolymers (binary or ternary in the case of partial replacement of the functional groups) which cannot be obtained by direct copolymerisation with ethylene.

The present review deals with copolymers of ethylene prepared by radical copolymerisation, and covers the literature up to September 1964. Work published before 1959 is mentioned only briefly, since this has been described in detail in monographs devoted to polyethylene[1,2], and more recent work is examined in greater detail.

II. GENERAL PROBLEMS OF THE COPOLYMERISATION OF ETHYLENE

Copolymers of ethylene, with such readily polymerised monomers as styrene, vinyl acetate, and acrylic acid, were first prepared as early as 1930,[3] i.e. before polymers of ethylene itself had been prepared. In the presence of peroxo-compounds under conditions of low pressure, a small quantity of ethylene was introduced into the polymer. However, the copolymerisation of ethylene with unsaturated compounds of different types[4] was described for the most part after the discovery of polyethylene. Styrene, isobutene, methyl acrylate, n-butyl acrylate, methyl methacrylate, vinyl acetate, butadiene, etc. were proposed as secondary components. The copolymerisation was carried out by a method analogous to that used for the polymerisation of ethylene, by the block method under conditions of high pressure (1000–2000 bars) and relatively high temperature (100–300°), in the presence of oxygen or peroxo-compounds as initiators[5-9]. It has been shown comparatively recently that it is possible to copolymerise ethylene under the influence of ionising radiation with alkenes[10], vinyl chloride, vinyl acetate, and carbon monoxide[11].

Colombo and Steinberg[12-14] describe the radiation copolymerisation of ethylene with a large number of monomers — propene, but-1-ene, *cis*- and *trans*-but-2-ene, isobutene, isoprene, vinyl chloride, chlorotrifluoroethylene, vinyl acetate, allyl acetate, allyl alcohol, acrylonitrile, methyl methacrylate, styrene, divinylbenzene, vinylpyrrolidone, methyl vinyl ketone, and carbon monoxide. In a number of cases, however, the data on the composition and properties of the resulting copolymers, given by Colombo and Steinberg, are of doubtful accuracy, since the copolymerisation was carried out to high degrees of conversion. On the basis of the data given below on the relative activities of monomers, it may be assumed that, in the case of copolymerisation with methyl methacrylate, methyl acrylate, vinylpyrrolidone, methyl vinyl ketone, and also possibly with propene and allyl acetate, the reaction products contained polyethylene.

Kolesnikov and his coworkers[15,16] showed that it is possible to copolymerise ethylene with certain monomers (vinyl chloride, styrene, vinyl acetate, acrylonitrile, and methyl methacrylate) under the influence of alkylborons.

The copolymerisation temperature for ethylene covers a very wide range, from -70° to 250°. The process is usually carried out at 180–250° in the case of initiation of copolymerisation by molecular oxygen[4] or within the range 50–150° for initiation by organic peroxides[5-9]. The use of γ-radiation[12] and alkylborons[16] makes it possible to carry out the copolymerisation at or below room temperature. The possibility is not excluded that at temperatures below 0° the process takes place partly or completely by an ionic mechanism. In particular, ethylene is known to polymerise by a cationic mechanism under the influence of ^{60}Co γ-radiation at -78°.[17,18]

The radical copolymerisation of ethylene is most frequently carried out at a pressure of $\sim$ 1000 bars[4,8,9]. The use of such high pressures is apparently necessary in order to produce a high concentration of ethylene to ensure sufficiently rapid reaction and to obtain copolymers of optimum