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POLYMER SYNTHESIS BY CYCLIC POLYMERISATION

S.G. Matsoyan

CONTENTS

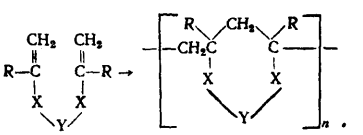
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I. INTRODUCTION

In connection with studies on the synthesis of polymers with valuable technical properties, in particular high thermal stability, there has been a considerable increase of interest in recent years in polymeric compounds containing cyclic groupings in the main chain [1-3]. At the present time extensive experimental data have been accumulated on the synthesis of various cyclic polymers, their structure, and their properties.

When the information available in the literature is generalised and systematised, it becomes clear that introduction of cyclic groupings, carbocyclic and heterocyclic units, into the main polymer chain can be achieved in three principal ways: by cyclic polymerisation, polycondensation, and chemical modification of polymeric compounds. Cyclic polymerisation can in turn be subdivided into two classes according to the mode of formation of the rings: chain polymerisation and stepwise polymerisation. The latter class includes polymerisation by the Diels–Alder reaction [4], thermal polymerisation of allene hydrocarbons [5], and others.

In the present review only cyclic polymers obtained by cyclic chain polymerisation are considered. In the field of cyclic polymerisation the so called intermolecular–intramolecular polymerisation of non-conjugated dienes has at present undergone the greatest development [6]. This type of cyclic polymerisation was discovered as a result of studies by several investigators [7-11], in particular Butler and coworkers [12,13]. It consists essentially in intramolecular ring closure of non-conjugated dienes, in particular 1,6-dienes, with simultaneous intermolecular chain growth, according to the following general mechanism:

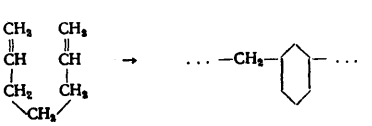


The polymerisation of other unsaturated systems, cyclodiene, triene, and vinylacetylene compounds and bifunctional compounds (dialdehydes, diepoxides) has also been investigated, using all known methods of initiation, with the aim of synthesising cyclic polymers. It was established that cyclic units in the polymer chain can form by intramolecular cyclisation of the monomer and interaction of two or several monomeric units of various types. For this reason, we shall give the name cyclic polymerisation to any type of polymerisation which leads to the introduction into the main polymer chain of cyclic groupings, regardless of the structure and nature of the monomer.

II. SYNTHESIS OF CARBOCYCLIC POLYMERS

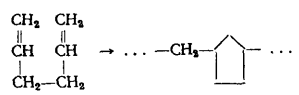
1. Polymerisation of Non-Conjugated Dienes.

A. Polymerisation of diene hydrocarbons. Marvel and Stille [14] were the first to show the possibility of the cyclic polymerisation of non-conjugated diolefins under the influence of complex metal alkyl catalysts. A solid, benzene-soluble polymer with cyclohexane rings in the chain, melting at 210–230° and having an intrinsic viscosity $[\eta] = 0.2–0.4$, was obtained from hepta-1,6-diene under the action of the $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$ catalytic system:



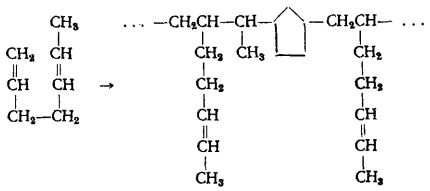
Rigid rubberlike polymers, the degree of cyclisation in the soluble fraction of which reaches 87%, are obtained under similar conditions from hexa-1,5-diene and 2,5-dimethylhexa-1,5-diene. Recently Makowski et al. [15] obtained in

the presence of aluminium triethyl and titanium tetrachloride a crystalline polyhexa-1,5-diene consisting of 1-methylene-3-cyclopentyl units:

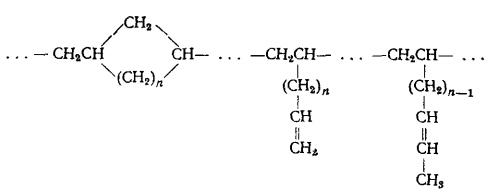


Its melting range extended to 146° and its intrinsic viscosity $[\eta]$ ranged up to 2.

The thermal stability of the cyclic polymers of hexa--1,5-diene, 2-methylhexa-1,5-diene, and hepta-1,6-diene was investigated by Anderson [16]. In the polymerisation of hepta-1,5-diene in the presence of aluminium triethyl and titanium tetrachloride a transparent rubberlike soluble product, consisting on average of 13 monomer units, was obtained [17]. It was established that the polymer contains units of two types in proportions of about 1 : 2: five--membered rings and branched groups with an internal double bond.



Marvel and Garrison [18] synthesised and studied the cyclic polymerisation of di-olefinic hydrocarbons with a long chain in the presence of Ziegler type catalysts. The degree of cyclisation of the soluble fraction of the polymers depends on the size of the rings formed (Table). The authors represent the structure of these polymers in the following way:

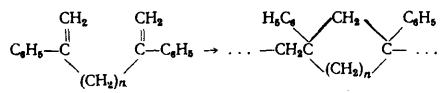


Field [19] studied the thermal polymerisation of 2,6-diphenylhepta-1,6-diene in the presence of free-radical initiators and anionic and cationic catalysts. According to his data, the polymerisation proceeds by a cyclic mechanism regardless of the method of initiation and leads to the formation of a polymer with six-membered rings in the chain. Using the method developed by Field, Marvel and Gall [20,21]

TABLE. Degree of cyclic polymerisation of di-olefins.

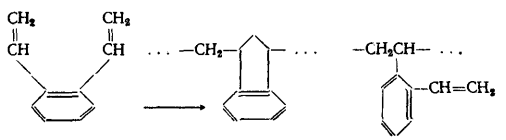
n in $CH_2{=}CH\diagdown\diagup(CH_2)_n$	Number of ring atoms	% of cyclic units in the soluble fraction of polymers	n in $CH_2{=}CH\diagdown\diagup(CH_2)_n$	Number of ring atoms	% of cyclic units in the soluble fraction of polymers
4	7	25	9	12	11
5	8	9	11	14	15
6	9	6	12	15	15
7	10	10	14	17	4
8	11	11	18	21	8

synthesised several phenyl-substituted diene hydrocarbons and studied their capacity for cyclic polymerisation:

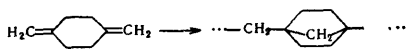


where n = 2, 3, 4.

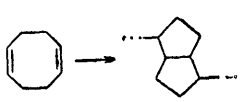
In the radical polymerisation of *o*-divinylbenzene [22] in benzene solution a soluble polymer (melting at 400° with decomposition) whose degree of cyclisation varied markedly with the reaction temperature and monomer concentration, was obtained. A kinetic equation for the calculation of the proportions of cyclic and vinyl polymerisation was derived.



Many investigators used cyclic polymerisation to prepare polymers with bicyclic bridge units. Ball and Harwood [23] obtained from 1,4-dimethylenecyclohexane under the action of gaseous boron trifluoride a soluble polymer (yield 85%, $[\eta]$ = 0.07) which does not melt up to 250°. The repeating unit in this polymer is methylene-1,4-bicyclo-[2,2,1]heptane:

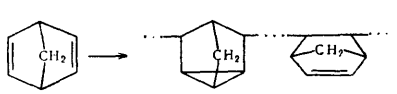


In the polymerisation of *cis,cis*-cyclo-octa-1,5-diene [24] under the action of the Ziegler catalyst a polymer (m.p. 100–180°, $[\eta]$ = 0.02–0.04) with a unit structure similar to bicyclo[3,3,0]octane was obtained:

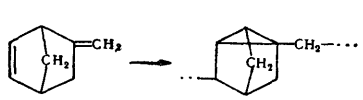


In the attempted preparation of a bridge-type polymer from cyclohexa-1,4-diene under similar conditions only rearrangement with formation of polycyclohexa-1,3-diene was observed.

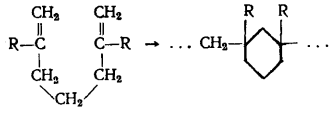
According to Zutty's data [25], in the presence of a free--radical initiator bicyclo[2,2,1]hepta-2,5-diene is converted into a low-molecular-weight soluble polymer containing both 3,5-disubstituted nortricyclene units and 5,6-disubstituted bicyclo[2,2,1]hept-2-ene units in the chain:



Bridge polymerisation [26] of 2-methylenenorborn-5-ene in the presence of aluminium tribromide leads to the formation of a polymer (m.p. 150–160°, $[\eta]$ = 0.3) whose units are produced by opening of both double bonds in the monomer with simultaneous formation of a bridge bond:

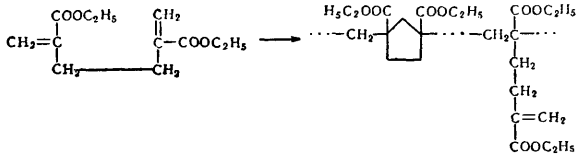


B. Polymerisation of substituted hepta--1,6-dienes, hexa-1,5-dienes, and penta--1,4-dienes. Marvel and Vest[27,28] studied the cyclic polymerisation of $\alpha\alpha'$-dimethylenepimelic acid and its methyl and ethyl esters, nitrile, and amide in the bulk, in solution, and in emulsion; in most cases soluble polymers were obtained, melting in the range 125–300° and having $[\eta] = 0.14–0.73$:

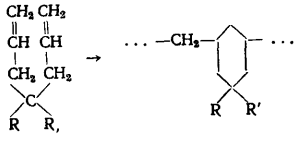


where R = COOH, $COOCH_3$, $COOC_2H_5$, CN, and $CONH_2$.

With the aim of synthesising soluble polymers having a high molecular weight, Milford[29] made a detailed study of the conditions of the cyclic polymerisation of the methyl ester and nitrile of $\alpha\alpha'$-dimethylenepimelic acid; on ultraviolet irradiation in solution in tetramethylenesulphone at 20° in the presence of benzoin as the photo-initiator, the corresponding cyclic polymers were obtained in 74–80% yield with $[\eta] = 2.03$ and 1.2 respectively. Radical polymerisation of 2,5-dicarbethoxyhexa-1,5-diene[28] in benzene solution leads to the formation of a cyclic polymer (m.p. 110–120°, $[\eta] = 0.21$) containing up to 10% of open-chain units:

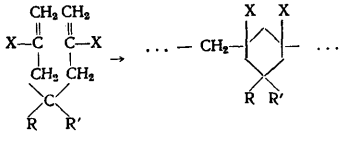


Matsoyan and his coworkers[30–32] studied the capacity for cyclic polymerisation of a number of 4-substituted hepta-1,6-dienes in the presence of radical initiators. The cyclic structure of the polymers obtained was demonstrated by chemical and spectroscopic methods:



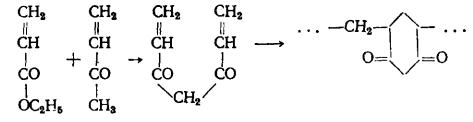
where R = H, R′ = COOH, $COOC_2H_5$, $COOC_6H_5$, $CONH_2$, $CON(CH_3)_2$, $CONHC_6H_5$, $COCH_3$, OH, $OCOCH_3$, $OCOC_6H_5$, Cl, CN; R = R′ = $COCH_3$; R = R′ = $COOC_2H_5$; R = $COCH_3$, R′ = $COOC_2H_5$; R = COOH, R′ = CN; R = $COOC_2H_5$, R′ = = CN.

These workers investigated the effect of the nature of the substituents (in positions 2, 4, and 6) on the cyclic polymerisation of substituted hepta-1,6-dienes[30–33]; the presence of methyl groups in positions 2 and 6 retards cyclic polymerisation while the presence of chlorine atoms sharply accelerates it. Under conditions of cyclic polymerisation 2,6-dichloro-4-substituted hepta-1,6-dienes undergo up to 70% dehydrochlorination:



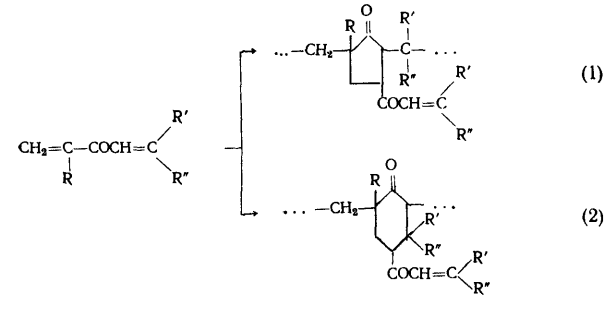
where X = CH_3 and R = R′ = $COOC_2H_5$; R = H, R′ = CN; R = $COOC_2H_5$, R′ = CN; R = COOH, R′ = CN; or X = Cl and R = R′ = $COOC_2H_5$; R = H, R′ = COOH; R = $COCH_3$, R′ = $COOC_2H_5$.

The mechanism of the cyclic polymerisation of some of the 4-substituted hepta-1,6-dienes described above was also studied by other investigators[34,35]. Jones[36] showed that in the Claisen condensation of ethyl acrylate with methyl vinyl ketone in the presence of sodium methoxide, a soluble coloured polymer (M = 2000) melting at 190° is formed instead of the expected diacryloylmethane. The author suggests that the actual product is a cyclic polymer of diacryloylmethane:



Somewhat later[37] in a detailed study of the condensation product described by Jones it was found that it is a copolymer of methyl vinyl ketone and diacryloylmethane. Bloomfield[38] synthesised the monomeric diacryloylmethane by the pyrolysis of the diene reaction adduct[39] and found that under the conditions used by Jones diacryloylmethane forms an insoluble three-dimensional polymer. However, later Marvel and coworkers[40] succeeded in obtaining in the presence of sodium methoxide at -75° a cyclic homopolymer of diacryloylmethane as a light yellow powder soluble in dimethylformamide.

Matsoyan and coworkers[41–43] showed that radical polymerisation of 1,4-dienes, substituted divinyl ketones, leads to the formation of solid soluble polymers containing cyclopentane or cyclohexane rings, depending on the structure of the monomers, instead of the expected four-membered rings; the polymer unit is formed by the cyclisation of two monomer molecules. The polymerisation of β-methylvinyl, di-(β-methylvinyl), β-t-butylvinyl, β-methylvinyl, α-methylvinyl β-methylvinyl, and ββ-dimethylvinyl α-methylvinyl ketones proceeds according to reaction (1), while dienes containing allyl groupings of the type $-COCH=CR-CH_2-$, β-ethylvinyl vinyl, β-n-propylvinyl vinyl, β-ethylvinyl β-methylvinyl, di-(β-ethylvinyl), and ββ-pentamethylene-vinyl vinyl ketones form polymers according to reaction (2):



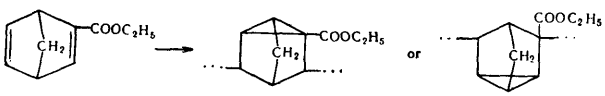
(1)

(2)

Arbuzova and Mosevich[44] obtained a soluble polymer ($[\eta] = 0.054$) with a cyclopentane ring in the chain by prolonged heating of dibenzylideneacetone at 130° in the presence of benzoyl peroxide.

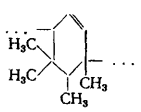
Radical polymerisation of 2-ethoxycarbonylbicyclo-[2,2,1]hepta-2,5-diene[45] yielded a soluble saturated polymer

with a vitrification temperature of 220° ([η] = 1.32–1.92). The principal structural units of this polymer are nortricyclenes:



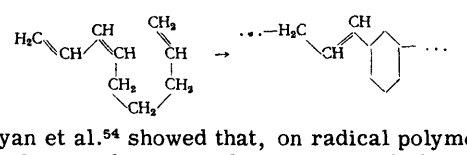
2. Polymerisation of Unsaturated Compounds of Other Types

Following the publication of studies on the cyclic polymerisation of non-conjugated dienes, reports appeared on the synthesis of carbocyclic polymers from unsaturated compounds of other types. Jones [46] studied the structure of soluble polymers of 2,6-dimethylocta-2,4,6-triene (allo-ocimene), whose polymerisation in the presence of cationic catalysts [47] has been known for a long time. On the basis of the data obtained and the known fact of the ease of cyclisation of allo-ocimene into α- and β-pyronenes [48,49], Jones suggested the following cyclic structure for polyallo-ocimene:

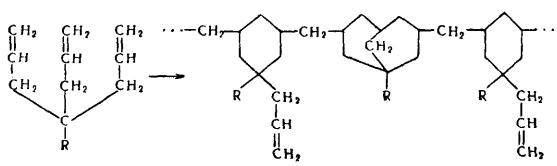


Marvel and coworkers [50,51] polymerised allo-ocimene under the action of anionic and cationic catalysts and made a detailed study of the structure of the polymers obtained. They found that the polymerisation of allo-ocimene proceeds mainly according to the usual linear mechanism, the degree of cyclisation being slight.

Butler and Brooks [52,53] showed that the polymerisation of triene hydrocarbons, *trans*-nona-1,3,8-triene, *cis*-nona-1,3,8-triene, and octa-1,3,7-triene, under the influence of aluminium triethyl and titanium tetrachloride leads to the formation of cyclic polymers as a result of simultaneous 1,2 and 1,4 intramolecular addition and chain growth:

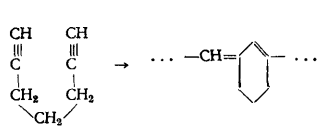


Matsoyan et al.[54] showed that, on radical polymerisation of branched trivinyl compounds such as triallylmethane derivatives, there is both monocyclic and bicyclic chain growth in proportions of 1 : 2:

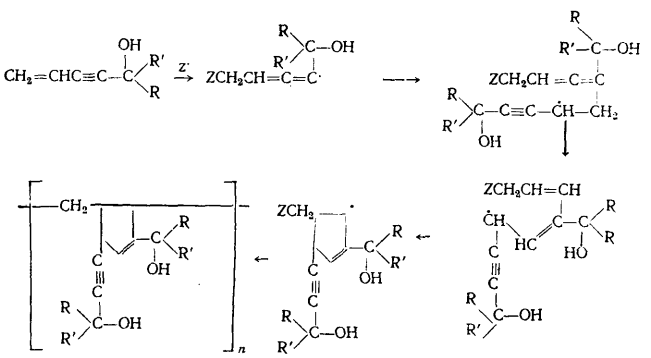


where R = OH, $OCOCH_3$, CN, $CONH_2$.

Stille and Frey [55] applied the cyclic diene polymerisation to hepta-1,6-diyne, octa-1,7-diyne, and nona-1,8-diyne. The polymers obtained in the presence of the Ziegler catalyst were brown or black in colour, which is probably due to double bond conjugation in the polymer chain:



Despite the view expressed in the literature [56], Matsoyan and coworkers [57–60] showed that the polymerisation of ethynylvinyl carbinols, both spontaneous and initiated, proceeds according to a chain mechanism and leads to the formation of high-molecular-weight soluble linear polymers, which are not cross-linked and are completely stable even on heating. According to the mechanism proposed [61,62], cyclic polymerisation of vinylacetylenic alcohols occurs as follows:



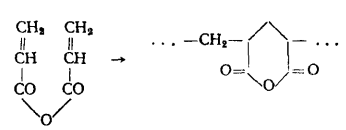
where R and R′ are aliphatic, alicyclic, aromatic and heterocyclic residues.

The kinetics of the cyclic polymerisation of ethynylvinyl carbinols have been studied [63,64]. Carbocyclic polymers of similar structure were obtained from ether derivatives of ethynylvinyl carbinols [65,66]. The possibility of the formation of linear-cyclic polymers from alicyclic [67] and aromatic [68,69] ethynylvinyl carbinol and also certain other vinylacetylenic compounds [70,71] has likewise been demonstrated. The dielectric properties of the cyclic polymer of dimethylvinylethynyl carbonil were studied by Kocharyan et al.[72]

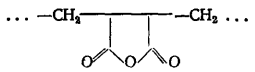
III. SYNTHESIS OF HETEROCYCLIC POLYMERS

1. Polymerisation of Non-Conjugated Systems Containing a Hetero-Atom

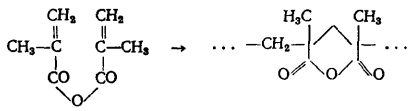
A. Polymerisation of oxygen-containing dienes. The formation of oxygen-containing heterocyclic polymers was first observed by Simpson and coworkers [7,9] in a study of the polymerisation of diallyl carbonate, oxalate, malonate, succinate, phthalate, glutarate, isophthalate, adipate, azelate, and sebacate, and also dimethylallyl carbonate and phthalate. It was found that the capacity of these esters for cyclisation does not always depend on the size of the ring formed (from eight- to seventeen-membered), although it might have been expected that the degree of cyclisation would decrease as the distance between the two allyl groups of the monomer increases. In order to obtain six-membered oxygen-containing heterocyclic polymers, Crawshaw and Butler [73] investigated almost simultaneously with Jones [74] the polymerisation of acrylic anhydride in the bulk and in solution using radical initiators and polymerisation regulators. The authors found that the chain units of the soluble polymers obtained consist of the anhydride of 5-methyleneglutaric acid:



Later Mercier and Smets[75,76] studied the kinetics of the cyclic polymerisation of acrylic anhydride and the structure of the polymer formed as a function of reaction temperature. At 115° and above the polymerisation leads to the formation of five-membered anhydride units in the chain:



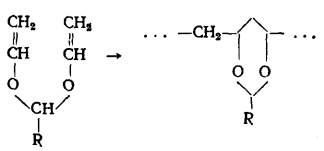
A cyclic polymer of methacrylic anhydride (m.p. 200°, $[\eta] = 0.6-0.8$) was obtained by Bresler et al.[77] in the radical polymerisation of the monomer in dimethylformamide:



The same polymer was synthesised by the authors by thermal dehydration of polymethacrylic acid.

In a study of the kinetics of the cyclic polymerisation of methacrylic anhydride Gibbs and Murray[78] found that the effective activation energy for the process is 23 kcal mole^{-1}. In order to confirm that the polymerisation of acrylic and methacrylic anhydrides proceeds accordingly to an intermolecular-intramolecular mechanism, Miyake[79] made a detailed study of the infrared spectra of the polymers. The stereochemical configuration of the cyclic polymers of the anhydrides of the unsaturated acids was determined[80-82]; it was shown by nuclear magnetic resonance that the poly(methyl methacrylate) obtained from the cyclopolymer of methacrylic anhydride has a stereoregular structure.

Matsoyan and Avetyan[83,84] demonstrated the possibility of obtaining acetals of poly(vinyl alcohol) directly from the monomers by the cyclic polymerisation of divinyl acetals. Later this reaction was used to prepare a wide variety of aliphatic[85-90], aromatic, and heterocyclic[91-95] poly(vinyl acetals):

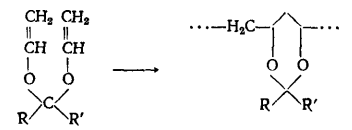


where R = H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, iso-C_4H_9, C_5H_{11}, C_6H_{13}, $CH_3O(CH_2)_2$, $C_2H_5O(CH_2)_2$, $C_3H_7O(CH_2)_2$, $ClCH_2CH_2O(CH_2)_2$, C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 2,4-$(CH_3)_2C_6H_3$, 2,5-$(CH_3)_2C_6H_3$, 3,4-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$, 2-$CH_3OC_6H_4$, 3-$CH_3OC_6H_4$, 4-$CH_3OC_6H_4$, 2-$C_2H_5OC_6H_4$, 2-$C_3H_7OC_6H_4$, 2-iso-$C_3H_7OC_6H_4$, 2-$C_4H_9OC_6H_4$, 2-iso-$C_4H_9OC_6H_4$, 2-$C_5H_{11}OC_6H_4$, 2-iso-$C_5H_{11}OC_6H_4$, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, α-$C_{10}H_7$, α-C_4H_3O.

The polymerisation of divinyl acetals occurs in the bulk and in solution in the presence of radical iniators and under the influence of ionic catalysts. It was found that in the cyclic polymerisation the steric configuration and the presence of an axis of symmetry in the monomeric divinyl acetal molecules are important.

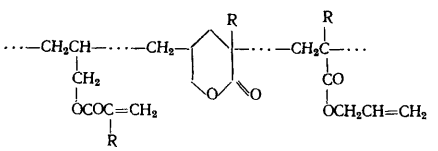
Arbuzova and coworkers[96-100] also studied the polymerisation of divinyl acetals; they obtained the cyclic polymers of the divinyl acetals of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and benzaldehyde. Sultanov and Arbuzova[101,102] established that, in contrast to divinyl acetals, allyl vinyl acetals and diallyl acetals give polymers in low yield, in which the fraction of cyclic units is small. It is interesting to note that ionic polymerisation of the divinyl acetals of formaldehyde[90,103] leads to the formation of only the cross-linked polymer, regardless of the reaction conditions.

The polymerisation of divinyl ketals[104], like that of divinyl acetals, leads to the formation of cyclic polymers containing, 1,3-dioxan rings:



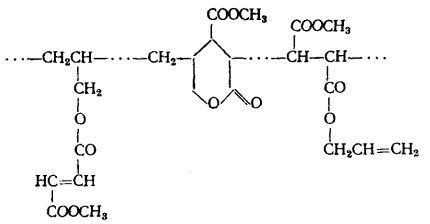
where R = R′ = CH_3; R = CH_3, R′ = C_2H_5; R,R′ = $(CH_2)_5$; R = R′ = C_6H_5.

The degree of cyclisation of asymmetric dienes, for example allyl esters of $\alpha\beta$-unsaturated acids, is as a rule low. Gindin et al.[105] indicated, in a discussion on the structure of the soluble polymers of allyl acrylate, the possibility that they have a cyclic structure. Several other workers[106-108] also obtained soluble polymers of allyl acrylate and allyl methacrylate, but the structre of the latter was not established. Schulz et al.[109] showed that, depending on the concentration of allyl acrylate in solution, the polymer contains at least 31% of six-membered lactone rings. In the radical polymerisation of allyl acrylate and allyl methacrylate[33] in dilute benzene solutions (5–10%) the yield of soluble polymers reaches 85%. By virtue of their considerable content of cyclic units, these polymers are relatively heat-resistant; the open-chain units contain both acryloyl and allyl bonds:



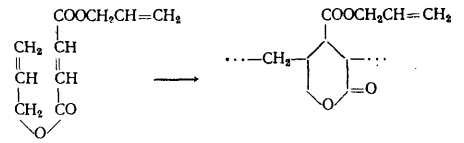
where R = H, CH_3.

The ionic polymerisation of allyl acrylate[110] under the influence of butyl-lithium proceeds exclusively at the acrylic double bond with formation of a non-cyclic polymer (m.p. 86–90°). Barnett et al.[111] studied the radical polymerisation of methyl allyl, methy-but-2-enyl, and methyl but-3-enyl esters of maleic and fumaric acids and found that the degree of cyclisation in the polymers obtained ($[\eta] = 0.036-0.072$) amounted to 23–60%. The authors believe that the possible cyclic units are six- or seven-membered lactone rings (in the case of but-3-enyl esters) and therefore the structure of poly(methyl allyl fumarate), for example, is represented as follows:

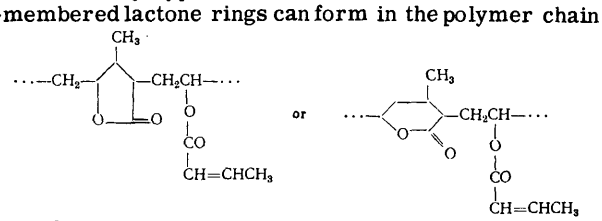


In the radical polymerisation of monoallyl esters of maleic and citraconic acids Arbuzova et al.[112] obtained cyclic polymers with a structure similar to that indicated

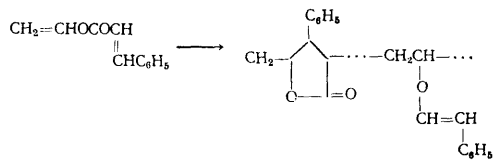
above. It was established that in the first stage of polymerisation of diallyl maleate [113] a soluble polymer is formed preferentially by a cyclic mechanism:



Rostovskii and Barinova [114] studied the radical polymerisation of vinyl crotonate in solution and obtained a soluble polymer ($[\eta] = 0.31$) containing about 50% of double bonds of the crotyl type. In their view both five-membered and six-membered lactone rings can form in the polymer chain:



In the polymerisation of vinyl *trans*-cinnamate in benzene solution in the presence of azoisobutyric acid dinitrile van Paesschen et al.[115] obtained a soluble polymer (yield 22–40%) which contained 80–85% of γ-lactone units and 15–20% of open-chain units:

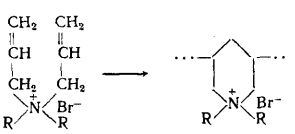


Roovers and Smets [116] studied the kinetics of the cyclic polymerisation of this monomer.

Barnett and Butler [117] investigated the polymerisation of allyl, β-methylallyl, γ-methylallyl, and propargyl vinylacetates and crotonates. The results showed that only allyl and β-methylallyl crotonates are converted into solid polymers (yield 10%, $[\eta] = 0.039–0.046$) with a degree of cyclisation of 25 and 31% respectively.

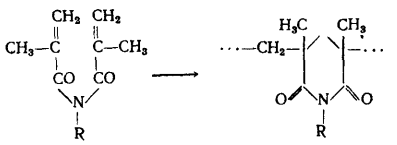
The cyclic polymerisation of non-conjugated oxygen-containing dienes was also investigated using the dimethacrylates of ethylene glycol and diethylene glycol as examples [118]. In contrast to the diallyl ester, the di-2-chloroallyl ester [33] readily forms a cyclic polymer which undergoes extensive dehydrochlorination as a result of the cyclisation of the monomer under the polymerisation conditions.

B. Polymerisation of nitrogen-containing dienes. The intermolecular-intramolecular polymerisation of non-conjugated dienes was in fact first used for the preparation of nitrogen-containing heterocyclic polymers. In their investigation of the radical polymerisation of unsaturated quaternary ammonium compounds Butler and coworkers [119–125] found that diallyldialkylammonium salts [12,13] form water-soluble polymers containing piperidine rings in the main chain:

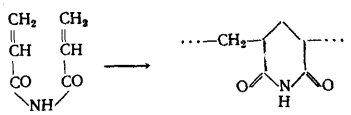


where R = H, CH_3, C_2H_5.

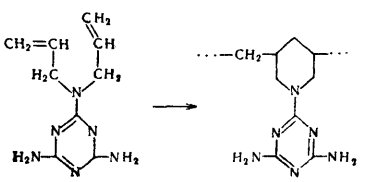
Sokolova and Rudkovskaya [126,127] synthesised six-membered nitrogen-containing polymers by the cyclic polymerisation of *N*-methyl- and *N*-ethyl-dimethacrylamides:



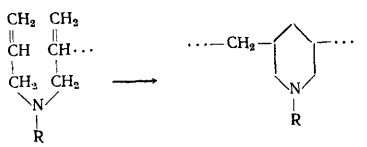
where R = CH_3, C_2H_5. In the polymerisation of *N*-acryloylacrylamide [128] a soluble polymer was obtained, whose chain units were identical with glutarimide:



Gibbs and van Densen [129] described cyclic polymerisation in the solid phase. On γ-irradiation (from a cobalt-60 source) of crystalline *NN*-diallylmelamine at room temperature, an acid-soluble polymer with a decomposition temperature of 250° and a molecular weight of 10 000–20 000 was obtained:



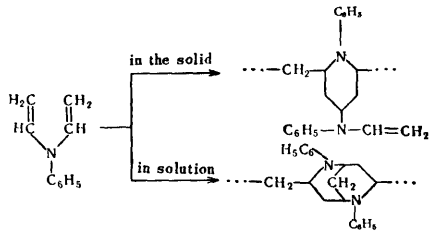
Matsoyan and coworkers [130] showed that introduction into diallylamine of polar substituents whose electron-acceptor group is lined directly with the nitrogen atom results in *N*-substituted diallylamine exhibiting a tendency towards radical polymerisation with formation of cyclic polymers containing piperidine rings:



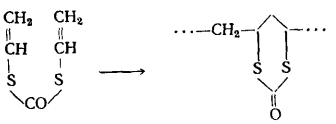
where R = CN, HCO, CH_3CO, C_2H_5CO, $ClCH_2CO$, CH_3OCO, C_2H_5OCO, C_6H_5CO, 4-$NO_2C_6H_4CO$, $C_6H_5SO_2$, 4-$CH_3C_6H_4SO_2$, $CSNHC_6H_5$. It was established that the capacity of *N*-substituted derivatives of di(methylallyl)amine [131] for cyclic polymerisation is much lower than that of the corresponding *N*-substituted diallyl derivatives. Similar cyclic polymerisation of *N*-diallyl compounds has been described by Ostroverkhov et al.[132]. In the polymerisation of allyl and ethyleneglycol esters of *N*-vinylcarbamic acid [109], *N*-allylacrylamide, and *N*-allylmethacrylamide [133] nitrogen-containing cyclic-linear polymers are also formed.

Chang and Price [133] described the synthesis of *NN*-divinylaniline and studied its polymerisation with the aid of an free-radical initiator. It was found that the polymeric unit forms as a result of the cyclisation of two *NN*-divinylaniline molecules and, depending on the method

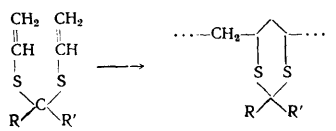
of polymerisation, the reaction leads to the formation of monocyclic or bicyclic units:



C. Polymerisation of dienes containing sulphur, silicon, phosphorus, and other elements. Ringsdorf and Overberger [134] studied the conditions of the polymerisation of *SS*-divinyl dithiocarbonate in the presence of a free-radical initiator and found that in dilute solutions a soluble cyclic polymer with a softening temperature of 300–310° is formed; a non-cyclic polymer obtained from the same monomer softens at 40–80°:



In the polymerisation of divinyl thioacetals and divinylmercaptans Matsoyan and Saakyan [135,136] obtained the sulphur analogues of polyvinylacetals in the form of elastic rubberlike substances. On hydrolysis these cyclic polymers converted into polyvinylmercaptan and on oxidation into the corresponding sulphones:

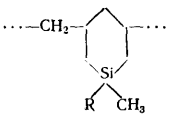


where R = R′ = H; R = H, R′ = CH_3; R = H, R′ = C_3H_7; R = R′ = CH_3. Ringsdorf and Overberger [137] also reported the cyclic polymerisation of the divinyl thioacetal of formaldehyde.

In contrast to diallyl sulphide and diallylsulphone, di-2-chloroallyl sulphide and di-2-chloroallylsulphone [33] are capable of polymerising in the presence of radical initiators with formation of cyclic sulphur-containing polymers which are extensively dehydrochlorinated under the reaction conditions.

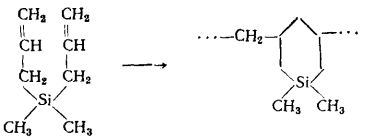
The possibility of the polymerisation of dialkenylsilanes in the presence of peroxide initiators was demonstrated by Korshak, Petrov, and coworkers [138–140]. The kinetics of the polymerisation of diallyldimethylsilane in the presence of t-butyl peroxide at 120–150° were investigated by Mikulasova and Hrivik [141]. Topchiev [142] demonstrated the possibility of the polymerisation of diallydimethylsilane and diallylmethylphenylsilane under the action of Ziegler type catalysts, but the structure of the products obtained, predominantly liquid, was not established.

Independently of Bogomol'nyi [144], Kolesnikov and coworkers [143] studied the polymerisation of diallyl derivatives of silicon. Under the action of the catalytic system $Al(C_2H_5)_3$–$TiCl_4$, diallyldiethylsilane gives a tetramer with six-membered cyclic units. Under similar conditions diallyldimethyl- and diallylmethylphenyl-silanes give rubber-like polymers, in the soluble fraction of which cyclic units with the following structure predominate:



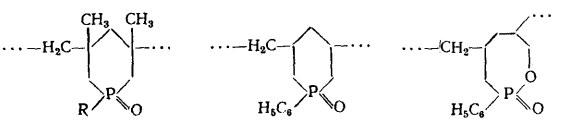
where R = CH_3, C_6H_5.

In a study of the polymer of diallyldimethylsilane obtained under the action of the $Al(iso\text{-}C_3H_7)_3$–$TiCl_4$ system, Marvel and Woolford [145] showed that the degree of cyclisation of the monomeric units in the polymer chain is 94%:



Butler and Stackman [146] studied the polymerisation of diallyldimethyl- and diallyldiphenyl-silanes with the aid of complex methal alkyl catalysts and obtained solid cyclic-linear polymers with m.p. 80–150° and $[\eta]$ = 0.065–0.13.

Berlin and Butler [147,148] studied the possibility of the cyclic polymerisation of phosphorus-containing non-conjugated dienes. They obtained soluble polymers (m.p. 85–185°, $[\eta]$ = 0.026–0.01) with a low content of residual double bonds on radical polymerisation in the solid state of methyl-, ethyl-, and dimethylallyl phenyl phosphine oxide, diallylphenyl phosphine oxide, and allyl phenyl allylphosphonate. The polymerisation proceeds by a cyclic mechanism with formation of phosphorus-containing heterocyclic polymers:

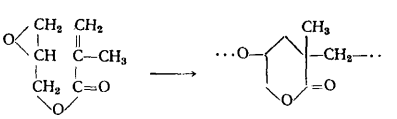


where R = CH_3, C_2H_5, C_6H_5. Unfortunately the structure of the soluble polymers of divinyl, diallyl and di(methylallyl) esters of various phosphorus acids has not been investigated, but is probably cyclic.

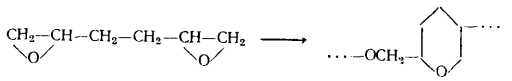
The synthesis of heterocyclic polymers from non-conjugated dienes containing other hetero-elements has been described in the literature — symmetrical diallyl compounds [143,149,150] in which the allyl groups are linked to the atoms of the following elements: Ge, Sn, Se, Ti, As, Pb, Zn, and others.

2. Polymerisation of Compounds of Other Types

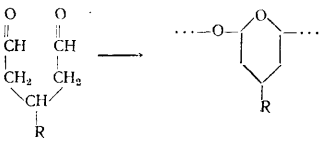
Arbuzova and coworkers [151,152] discovered the formation of a new type of cyclic polymers, from the glycidyl esters of acrylic and methacrylic acids. According to their data, both the epoxy-ring and the double bond of the monomer participate in ionic polymerisation [boron trifluoride etherate, aluminium trichloride], in contrast to radical polymerisation, with formation of cyclic units in the main polymer chain:



Stille and Culbertson [153] found that, under the action of the catalytic system PF_5–H_2O or $Zn(C_2H_5)_2$–H_2O, 1,2,5,6-diepoxyhexane polymerises with formation of a soluble polymer consisting of tetrahydropyran structural units:

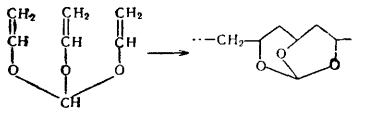


Under similar conditions 1,2,4,5-diepoxypentane yields insoluble polymers. A number of investigators have applied cyclic diene polymerisation to dialdehydes. In the polymerisation of glutaric aldehyde [154,155] in the solid state without initiator or in solution (in toluene) under the influence of various catalysts [BR_3.$(C_2H_5)_2O$, $Al(iso\text{-}C_3H_7)_3$, and others] soluble polymers with a small content of aldehyde groups are obtained. Infrared spectra of polyglutaraldehyde and also the polymers of β-methyl- and β-phenyl-glutaric aldehyde [156] show that the polymerisation involves intermolecular-intramolecular interaction of the two carbonyl groups of the monomers with formation of tetrahydropyran rings in the polymer chain:

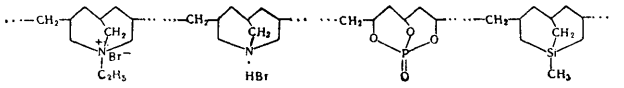


where R = H, CH_3, C_6H_5.

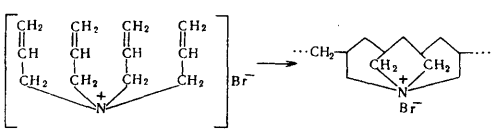
Matsoyan and coworkers [54] polymerised trivinyl orthoformate in solution in the presence of radical initiators and obtained a soluble bicyclic polymer (m.p. 250–260°) which is an ester derivative of poly(vinyl alcohol) and orthoformic acid:



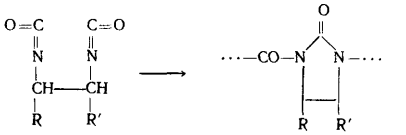
The possibility of the formation of nitrogen-, silicon-, and phosphorus-containing bicyclic polymers from branched trivinyl compounds has been demonstrated with triallylethylammonium bromide [157], triallylammonium bromide [54], trivinyl phosphate [54], and triallylmethylsilane [157] as examples. The chain units of the soluble polymers obtained have the following structure:



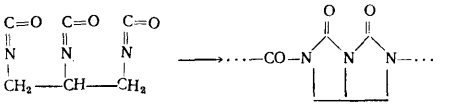
Trifan and Hoglen [157] have indicated that in the polymerisation of tetra-allylammonium bromide in dilute aqueous solution in the presence of t-butyl hydroperoxide (0.3%) a soluble polymer with tricyclic units in the main chain is formed:



King [158] polymerised aliphatic 1,2-diisocyanates in dimethylformamide solution in the presence of sodium cyanide and obtained cyclic-linear polymers between 290° and 365° and soluble in sulphuric acid, nitromethane, etc. According to his data, the cyclic polymerisation proceeds as a result of intermolecular-intramolecular interaction between the two nitrogen–carbon double bonds in the monomer:



where R = R′ = H; R = H, R′ = CH_3; R, R′ = $(CH_2)_4$. Under similar conditions glyceryl triisocyanate yields a bicyclic polymer melting at 365–400°:

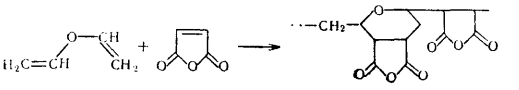


IV. SYNTHESIS OF CYCLIC COPOLYMERS

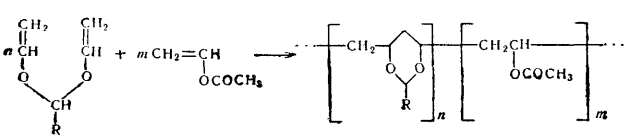
Even before the discovery of the cyclic polymerisation of non-conjugated dienes, the copolymerisation of vinyl monomers with isolated dienes was known; this reaction is widely used in the manufacture of cross-linked polymeric materials and cast articles.

Milford [29] studied the radical copolymerisation of 2,6-di(methoxycarbonyl)hepta-1,6-diene with acrylonitrile in solution and found that, when the concentration of the monomer mixture in the system is not higher than 10%, soluble linear copolymers with substituted cyclohexane rings in the chain are formed.

Butler [159] described the cyclic copolymerisation of vinyl ether, divinyl sulphone, and dimethyldivinylsilane with maleic anhydride, diethyl maleate, dimethyl fumarate, and vinyl acetate. Using vinyl ether and maleic anhydride as an example, Butler represents the formation of cyclic polymers in the following way:

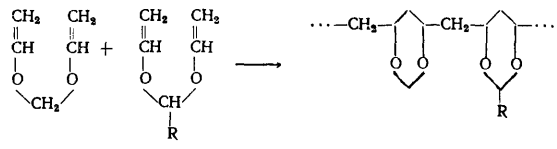


Matsoyan and coworkers [160–163] showed that the radical copolymerisation of the divinyl acetals of formaldehyde, acetaldehyde, butyraldehyde, isobutyraldehyde, and isovaleraldehyde with vinyl acetate proceeds by a cyclic mechanism; in the copolymer the divinyl acetal units form 1,3-dioxan rings. It was found that, whatever the molar proportions of the components and whatever the degree of the reaction, this type of copolymerisation leads to the formation of azeotropic copolymers, whose compositions are identical with those of the initial mixtures:

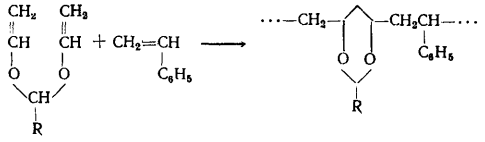


The possibility of cyclic copolymerisation of two diene monomers, forming rings on polymerisation, has been demonstrated [85] using the copolymerisation of the divinyl

acetal of formaldehyde with the divinyl acetals of acetaldehyde and butyraldehyde as examples[85]:

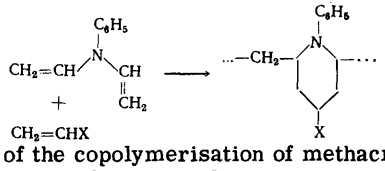


The copolymerisation of aliphatic divinyl acetals with styrene in the presence of benzoyl peroxide leads to the formation of the corresponding cyclic copolymers[164]. This reaction makes it possible to introduce simply and conveniently divinyl acetal units into the polystyrene chain:



Cyclic copolymers of similar structure were also obtained in the copolymerisation of the divinyl acetals of formaldehyde, acetaldehyde, and butyraldehyde with 2-methyl-5--vinylpyridine[165]. The possibility of cyclic copolymerisation of the divinyl acetal of butryaldehyde with monomers incapable of homopolymerisation — dimethylcrotonoyl carbinol and dimethylcrotonoylmethyl acetate — has been investigated[165]. It was found that in the presence of the cyclic divinyl butyraldehyde acetal these monomers are capable not only of copolymerisation but also of homopolymerisation.

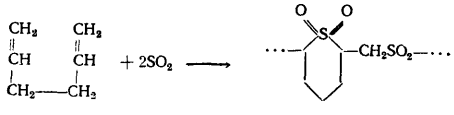
According to the data of Chang and Price[133], the copolymerisation of *NN*-divinylaniline, divinyl sulphone, and vinyl ether with styrene, *p*-methylstyrene, methyl methacrylate, etc. leads to the formation of six-membered cyclic groupings, each comprising one molecule of the diene and the vinyl component. Thus the cyclic copolymerisation of *NN*-divinylaniline with a vinyl monomer proceeds according to the following mechanism:



In a study of the copolymerisation of methacrylic anhydride with methyl methacrylate, styrene, acrylonitrile, etc. Hwa and Miller[166] found that soluble cyclic-linear copolymers are formed only when the reaction mixture is very dilute and when the degree of reaction is low. They showed that the usual equations for a binary system of vinyl monomers are applicable in the calculation of the composition of the cyclic copolymer when the degree of cyclisation of the non-conjugated diene component is relatively complete.

Michelotti[167] reported the possibility of cyclic copolymerisation of diallyl-2,3-epoxypropylamine with styrene.

Stille and Thomson[168] showed that the copolymerisation of hexa-1,5-diene with sulphur dioxide leads to the formation of a cyclic copolymer containing pentamethylene sulphone rings; the ratio of the initial components in the soluble part of the copolymer (m.p. 320–350°) is 1 : 2 respectively:



Roovers and Smets[116] established that the copolymerisation of vinyl *trans*-cinnamate with vinyl acetate, vinylpyrrolidone, methyl methacrylate, and styrene results in chain growth of the vinyl type due to the ester group of the diene as well as the cyclisation of the diene monomer into γ-lactone rings.

Avetyan et al.[169] showed that, in addition to the usual vinyl copolymerisation, cyclisation with formation of cyclopentanone rings in the main copolymer chain proceeds in the radical copolymerisation of isopropenyl propenyl ketone and isobutenyl vinyl ketone with acrylonitrile, vinylidene chloride, and 2-methyl-5-vinylpyridine. In the presence of radical initiators dibenzylideneacetone and maleic anhydride form an unsaturated cyclic-linear copolymer[44]. Matsoyan and Morlyan[170] studied the copolymerisation of ethynyldimethylvinyl carbinol with styrene, acrylonitrile, vinylidene chloride, methyl methacrylate, and vinyl acetate in the presence of benzoyl peroxide. They showed that the fraction of the copolymer consisting of the ethynyldimethylvinyl carbinol units contains cyclic units, like the homopolymers of ethynylvinyl carbinol[62,63].

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The foregoing review shows that cyclic polymerisation constitutes a new and rapidly developing field in polymer chemistry. Cyclic polymerisation makes it possible to prepare fundamentally new types of polymeric compounds with a wide variety of cyclic groupings in the chain, which were previously unobtainable; for this reason, synthesis of polymers and copolymers by cyclic chain polymerisation has been attracting recently the attention of a wide circle of investigators. There is no doubt that in future still further varieties of cyclic polymerisation will be discovered and that this method of synthesising polymeric compounds is one of the important means of obtaining polymers with valuable technical properties.

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THE SYNTHESIS OF MACROMOLECULAR COMPOUNDS BY RADIATION POLYMERISATION

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INTRODUCTION

At the present time, polymerisation is initiated chiefly by chemical methods in which the monomers or their solutions are treated with initiators for polymerisation taking place by a radical mechanism, or catalysts for ionic polymerisation. The use of thermal and photochemical method of initiation is limited — for the first because of the unfavourable conditions for the development of chains at elevated temperatures and the secondary processes which take place, and for the second because of the low efficiency and the complexity of the technological layout, associated chiefly with the influence of the optical properties of the medium on the course of photochemical reactions.

Recently, the attention of many research workers has been drawn to a new method of polymerisation — radiation polymerisation — in which the chain process is initiated by the action of ionising radiation. The first observations of the formation of polymeric (resinous) substances under the influence of the radiation from radium and radon were made at a very early date, but the development of radiation polymerisation as an independent branch of the chemistry of macromolecular compounds is a recent phenomenon. It appears that in a few years this new method will be recognised as an effective industrial method for the synthesis of certain polymeric products.

Problems of radiation polymerisation have been examined in a number of general papers and reviews[1-17], which give data characterising chiefly the fundamental features of the method, in particular the mechanism of radiation-chemical initiation, the influence of various factors (including such specific factors as the dose and dose rate) on the reaction rate, sensitisation in multicomponent systems, polymerisation in inclusion compounds, etc. Special reviews devoted to radiation polymerisation in the solid phase[18-23] and a review of the patent literature[24] have been published. No systematic review of data on the use of radiation-chemical initiation for the polymerisation of various monomers according to classes has