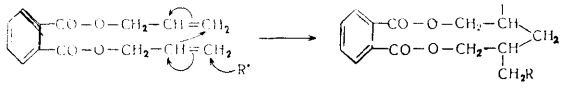
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Institute of Chemistry,
East-Siberian Branch of the Siberian
Section of the USSR Academy of Sciences

POLYMERISATION OF UNCONJUGATED DIENES

G. S. Kolesnikov and S. L. Davydova

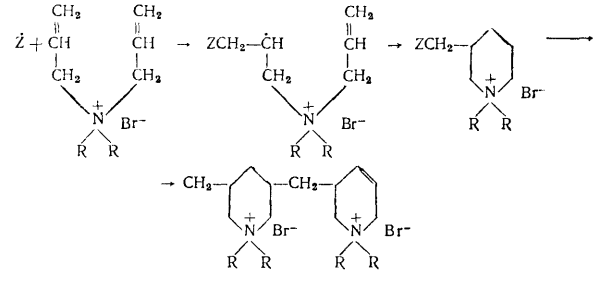
Ring closure during the polymerisation of compounds containing isolated double bonds was first proposed by Simpson[1] to explain the structure of the soluble poly(diallyl *o*-phthalate), obtained at low degree of polymerisation. A year later Howard[2] demonstrated the "intramolecular cross-linking" of some of this ester, during peroxide-induced polymerisation, giving an eleven-membered ring, and possibly some of the ten- and twelve-membered ring compounds:



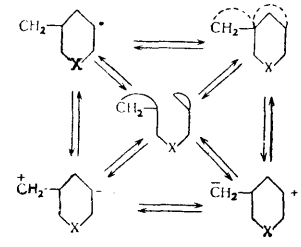
Later, Simpson and Holt[3,4] investigated the polymerisation, under the same conditions, of the diallyl and di-β-methylallyl esters of oxalic, malonic, succinic, glutaric, adipic, azelaic, sebacic, carbonic, and the three phthalic acids.

Polymers from such esters have recently been shown to be typical of many polymers from compounds containing two isolated double bonds, being abnormally soluble in organic solvents and showing little unsaturation. Many such polymers turn into equally soluble transparent plastics at high temperature and pressure.

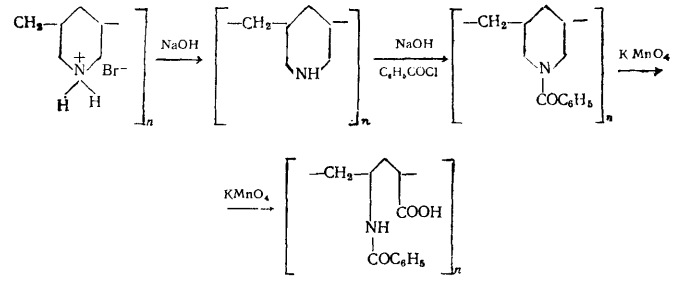
Butler and his coworkers[5-13] investigated the free-radical polymerisation of many allyl and methylallyl derivatives of quaternary ammonium salts, with the initial purpose of making strongly basic ion-exchange resins. Monoallyl derivatives did not polymerise at all, tri- and tetraallyl derivatives gave insoluble three-dimensional polymers, but the polymers from diallyl derivatives dissolved readily in water and ethanol[10-12]. This refuted the general assumption that polymers from monomers with one double bond are relatively soluble, while those from monomers with two or more double bonds are sparingly soluble or insoluble[15]. The effects of the initiator type and concentration, the nature of the anion, the amount of solvent, and the presence of oxygen, etc., on the polymerisation of compounds containing two double bonds, and the hydrogenation of polymers, were also studied[5-14]. Molecular-weight determination was complicated by the polyelectrolyte nature of the polymers. Butler and Angelo[11] found that polymerisation is most efficient if initiated by 2–3 wt.% of t-butyl peroxide or an azo compound, and continued for 48 h at about 60°. They concluded that free radicals initiate polymerisation of the diallyl derivatives to soluble products of relatively low molecular weight and a low degree of unsaturation, the mechanism they suggested involves radical chain propagation by a succession of intra- and intermolecular steps. Methylene and 3,5-disubstituted piperidinium groups alternate in the saturated, unbranched chain of the product, five- and six-membered rings being preferentially formed:

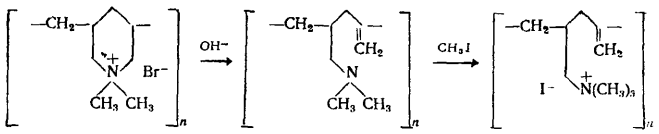


Butler[14] explained the strong tendency of 1,6-dienes to polymerise, in comparison with compounds containing only one double bond, in terms of mesomerism:

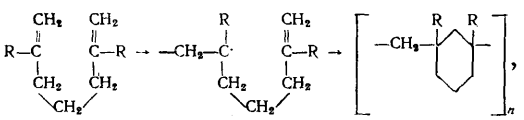


In order to establish the structures of the polymers, Butler et al.[13] investigated the degradation products of poly(diallylammonium bromide) and poly(diallyldimethylammonium bromide):

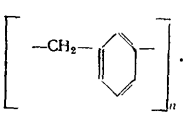




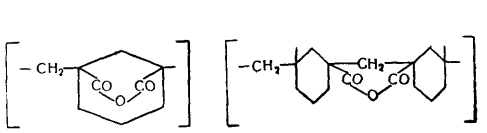
Recently Butler's terminology has gained wide acceptance, such terms as "cyclopolymerisation", "cyclopolymers", "cyclocopolymers", and "cyclocatalysts" appearing in the literature, and his mechanism has been applied to many other polymerisations, involving different initiators and catalysts, and producing chains containing rings of five or more atoms. Marvel and Vest[16] confirmed Butler's mechanism by obtaining polymers, soluble in organic solvents, from α,α'-dimethylenepimelic acid, its methyl and ethyl esters, and, recently, its nitrile and amide. Free-radical initiation was successful with solids, solutions, and emulsions. The authors' proposed mechanism is:



where R = COOH, $COOCH_3$, $COOC_2H_5$, CN, or $CONH_2$. The ring was aromatised by heating with potassium perchlorate in a sealed tube:



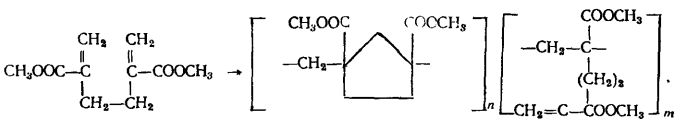
Polymerised dimethyl α,α'-dimethylenepimelate had an intrinsic viscosity, $[\eta]$, of 0.73 in chloroform, m.p. 300° (measured in a sealed tube, as for all polymers described), and a molecular weight of $2-3\times10^5$. For the polymerised diethyl ester, m.p. 125°–135°, $[\eta]$ was 0.14 in chloroform. The infra-red spectra of both polymers indicated negligible unsaturation. The products of dehydrogenation with potassium perchlorate showed infra-red peaks at 1620, 1595, and 1500 cm^{-1} and ultra-violet peaks at 255 and 240 mμ, characteristic of aromatic compounds and supporting the accepted mechanism of polymerisation[11]. Heating the poly(diethyl ester) at 300° caused no depolymerisation, a new soluble polymer forming, with infra-red bands characteristic of the acid-anhydride group. The authors suggested possible structures for the chain units:



The dinitrile of α,α'-dimethylenepimelic acid underwent free-radical polymerisation in dimethylformamide[17]. The polymer had an intrinsic viscosity of 0.655 in that solvent. Its unsaturation was virtually limited to the cyano groups, and it was more stable to heat than most polynitriles[18]; it darkened after several hours above 300°, but 80% of the polymer remained.

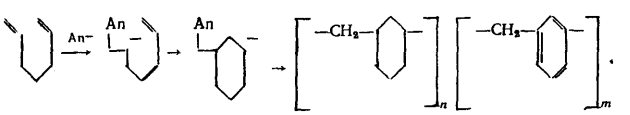
The polymer from the corresponding diamide[17] was exceptional in being insoluble in organic solvents. Any infra-red absorption bands due to the C=C bond were masked by those of the carbonyl group. The authors supposed the polymer to be cyclic, attributing its insolubility to extensive hydrogen bonding and not to a three-dimensional structure. The diamide, like the dinitrile, forms partially soluble copolymers with acrylonitrile or methyl acrylate; these are saturated, and stable up to about 250°.

Under similar conditions Marvel and Vest[17] obtained from dimethyl α,α'-dimethyleneadipate a polymer with little residual unsaturation, melting between 110° and 120°, of intrinsic viscosity 0.21 in benzene. 10% of the monomer units were in the form of open chains, and the rest as five-membered rings:

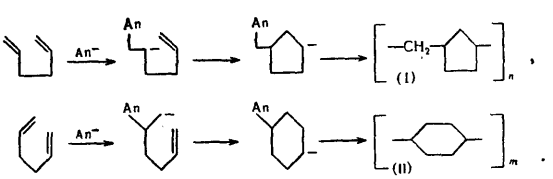


Marvel and Vest[17] noted that only soluble polymers are formed from emulsions or solutions of unconjugated dienes, but that polymerisation of the solid always gives some insoluble product.

In 1958 Marvel and Stille[19,20] polymerised hepta-1.6-diene with a mixed catalyst of aluminium isobutoxide and titanium tetrachloride. The product, of high molecular weight, melted at 210°–230°, dissolved readily in benzene, and formed films from this solvent. For $Al(iso\text{-}C_4H_9)_3$: $TiCl_4$ ratios of 1 : 1 and 1 : 3, $[\eta]$ = 0.2 and 0.4 respectively. Infra-red spectra showed that only 4–10% of the monomer units retained one of the two double bonds. Infra-red and ultra-violet spectra showed the product of degradation with potassium perchlorate (e.g. at 390° for 16 h in a sealed tube) to contain *meta*-substituted aromatic rings:



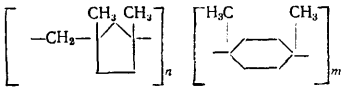
Hexa-1,5-diene gave a rubber-like polymer melting at 85°–90°, soluble only to the extent of 40 wt.% in benzene; for the soluble fraction, $[\eta]$ = 0.23. Comparison of the infra-red spectra of the monomer and the soluble polymer fraction showed that 5–8% of the monomer units retained one double bond. Of the structures proposed by the authors, (II) is believed the less likely, on account of the unstable anionic intermediate:



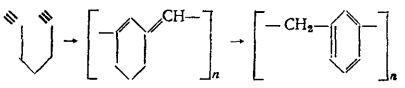
2,5-Diphenylhexa-1,5-diene gave similar soluble polymers of low molecular weight when polymerised by cationic or free-radical initiators[21].

Although 2,5-dimethylhexa-1,5-diene is one of the α,α'-disubstituted dienes, not polymerised by complex metal alkyl catalysts, Marvel and Stille[19] obtained from it a polymer of relatively low molecular weight (10 000), soluble in some organic solvents, melting at 80°–85°, and of intrinsic viscosity 0.1. Of the monomer units, 3–13%

retained their unsaturation. Two structures were proposed:

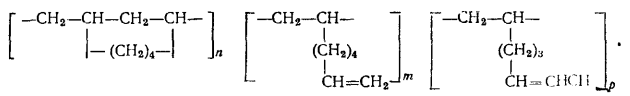


On thermal, free radical, cationic, or anionic initiation, 2,6-diphenylhepta-1,6-diene gave soluble polymers melting between 140° and 300°, for which $[\eta] = 0.19-0.49$.[21] From hepta-1,6-diyne and a Ziegler catalyst, Stille[21] obtained polymers of molecular weight 10 000–20 000, which were converted to polybenzyl on heating with palladised charcoal:

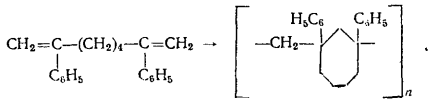


A British patent[22] describes polymerisation by complex metal alkyl catalysts of penta-1,4-diene, hexa-1,5-diene, octa-1,7-diene, and deca-1,9-diene, but does not indicate structures. A Belgian patent[23] describes copolymerisation of penta-1,4-diene, hexa-1,5-diene, and octa-1,4,7-triene with several olefines, using the same catalysts.

Marvel and Garrison[24] studied the polymerisation by complex metal alkyl catalysts of dienes of type $CH_2=CH-(CH_2)_n-CH=CH_2$, where n = 4, 12, 14, and 18. Soluble and insoluble fractions were obtained. The former was of low molecular weight and had an intrinsic viscosity of ~0.1; the latter was distinctly unsaturated and swelled considerably in benzene, indicating few cross-linkages. Extension of the polymerisation time gave only three-dimensional structures. Quantitative infra-red spectrometry and bromination showed that the soluble polymer fraction contained cyclic, vinyl, and vinylidene units:



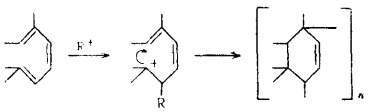
Polymerisation of, e.g. 2,7-diphenylocta-1,7-diene by a Ziegler or cationic catalyst apparently gave, at a low extent of polymerisation, cyclic polymers[21]:



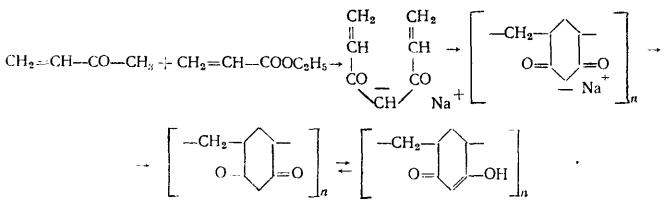
Marvel concluded that unconjugated dienes with three atoms separating the double bonds usually give soluble linear polymers with a six-membered ring unit. Fewer separating atoms may lead to a five-membered ring unit, but this is formed with difficulty and is accompanied by unsaturated open chain units. More than three separating atoms cause seven-membered rings to be formed, but with even more difficulty. Rings of more than seven members are very uncommon.

The conversion of *allo*ocimene (2,6-dimethylocta-2,4,6-triene) by various catalysts to soluble polymers of still unknown structure is well established[25-27]. Marvel and his coworkers[28] recently catalysed this polymerisation, with aluminium isobutoxide and titanium tetrachloride, in heptane at 15°. The amorphous, fibrous product, of intrinsic viscosity 1.0–1.2, melted between 120° and 154°, dissolved in organic solvents, and formed fairly strong films at 150° and 35 kg cm^{-2}. Traces of phenyl-β-naphthylamine reduced its tendency to atmospheric oxidation. Above 200° the polymer reverted to *allo*ocimene in 70% yield; infra-red spectra showed it to contain double bonds with a *trans*-configuration.

Jones[29] polymerised *allo*ocimene, by means of boron trifluoride etherate, to a soluble polymer, softening at 68°–70° and melting at 85°–87° and 70 kg cm^{-2} pressure; extrusion of the melt gave brittle fibres. The author suggested that one double bond takes part in the polymerisation and proposed a cationic mechanism:

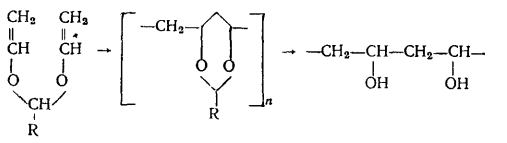


Jones[30] did not obtain diacroylmethane or its sodium salt from the Claisen condensation of methyl vinyl ketone with ethyl acrylate, since a polymer of the salt was formed at once, and was converted by acetic acid to polydiacroylmethane, made up of alternating methylene and dihydro-4,6-dihydroxy-*m*-phenylene units:



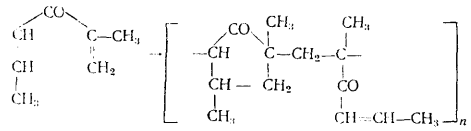
This polymer is soluble and of low molecular weight (2000), melts at 190°, and readily forms films; its infra-red spectrum indicates little unsaturation. Potentiometric titration showed that 48% of the polymer was present as enol, and polymeric azo dyes could be prepared from it. As the polymerisation proceeds at ordinary temperatures in the presence of air and free-radical inhibitors, the author inferred an anionic mechanism.

Divinylacetals have recently been converted to cyclic polymers[31-33] by peroxide initiators. Polydivinylformal is a white powder melting between 85° and 120°, and polydivinylbutyral is colourless and rubber-like. All the polydivinylacetals obtained dissolve readily in most organic solvents and show their saturation by not reacting with hydrogen or bromine. Hydrolysis gives polyvinyl alcohol:



Copolymers of divinylacetals with styrene, vinyl acetate, or acrylonitrile are soluble and fusible, with strong adhesive properties; the copolymer of divinylbutyral and styrene melts between 105° and 116°. Cyclic copolymerisation of two divinyl monomers is possible, as was shown for divinylformal and divinylacetal[32]. Matsoyan and Avetyan[34] also investigated the radical polymerisation of 2-methylhexa-1,4-diene-3-one, alternate molecules appa-

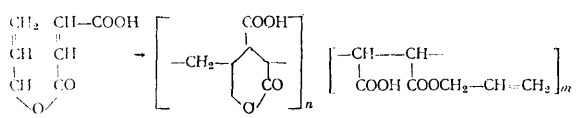
rently undergoing vinyl polymerisation of the isopropenyl group or ring closure:



The authors attribute this mechanism to steric hindrance of the formation of a complete chain of five-membered rings. The polymer is a white powder melting at 145°–150°, readily soluble in organic solvents, and of intrinsic viscosity 0.11 in benzene. Ozonolysis and bromination indicated about 25% unsaturation, relative to the monomer. 2,5-Dimethylhexa-1,4-diene-3-one polymerises in the same way.

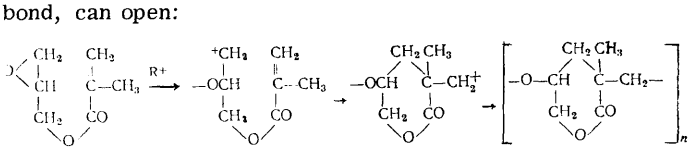
Arbuzova and her coworkers[35] obtained linear polymers (in reactions without solvent) from radical initiators and pure divinylformal, divinylacetal, and divinylbutyral; cyclic structures were indicated by analytical data and physical properties. With similar initiators, divinylbenzal gave a polymer of low molecular weight, in which methylene groups alternate with 3-phenyl-2,4-dioxacyclohex-1,5-diyl groups[36].

Arbuzova and Rostovskii[37,38] studied the cyclic polymerisation of a series of symmetrical and unsymmetrical 1,5- and 1,6-dienes, such as divinylacetals, monoallyl esters of unsaturated acids, and vinyl crotonate. Polymerisation (without solvent) of pure monoallyl maleate and citraconate in the presence of peroxide initiators gave 40–50% yields of linear polymers, soluble in dioxan, dimethylformamide, and other organic solvents; that from the maleate had a molecular weight of 15 000, determined from the rate of sedimentation, and an intrinsic viscosity of 0.156. About 25% of the units contained allylic double bonds:



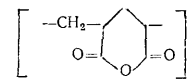
Azo-compound-initiators cause solutions of vinyl *trans*-crotonate and cinnamate to give linear polymers; one specimen of polyvinyl crotonate, of intrinsic viscosity 0.31, contained five- and six-membered lactone and ester units.

Arbuzova and Efremova[39] established a new type of cyclic polymerisation by means of the action of ionic catalysts on glycidyl esters of acrylic and methacrylic acids. The ethylene oxide (oxiran) ring, as well as the double bond, can open:



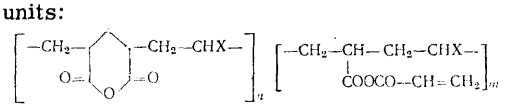
Glycidyl methacrylate was converted by boron trifluoride etherate and hydroquinone to a soluble polymer of low molecular weight. The radical-initiated polymerisation of glycidyl esters of unsaturated acids involves only the double bond[40].

Crawshaw and Butler[41] obtained polymers from acrylic anhydride on radical initiation in solution; these dissolved in organic solvents, and had molecular weights from several thousand to 95 000. The infra-red spectrum of the hygroscopic white powder produced indicated inappreciable unsaturation, and the authors consider the structural unit to be derived from α-methylglutaric anhydride:



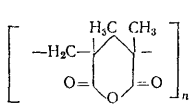
The polymer was hydrolysed to a polyacrylic acid of more regular structure than that of specimens made by radical-initiated polymerisation of acrylic acid.

From acrylic anhydride and radical initiators in organic solvents, Jones[42] obtained a linear polymer of molecular weight 200 000 which was hygroscopic and readily soluble in polar organic solvents such as dimethylformamide, γ-butyrolactone, *N*-methylpyrrolidone, and dimethyl sulphate. Acrylic anhydride is often considered as a cross-linking agent, copolymerising with other vinyl monomers[42,43]. In its homopolymerisation all the vinyl groups are equivalent, and cyclise and polymerise readily (cyclopolymerisation). On addition of a monomer of different reactivity, cyclic polymerisation is reduced and is accompanied by formation of up to 50% of three-dimensional non-cyclic units:



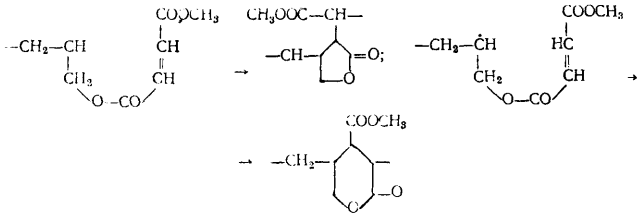
By controlling acrylic anhydride polymerisation with compounds such as trimethylamine or dimethyl sulphide, Jones[42] obtained a linear polymer of high molecular weight, and also a polymer of molecular weight 20 000, soluble in ethanol and dioxan, with considerable unsaturation evidently due to end groups, and readily converted to transparent granules and films at 180° and 1750 kg cm^{-2} pressure. The polymer enters into many reactions characteristic of anhydrides, its reactivity decreasing as its molecular weight increases, possibly on account of intermolecular steric hindrance. Hydrolysis with water for some days at room temperature made films of linear polyacrylic anhydride identical with those of polyacrylic acid.

Using Butler's method[41], Bresler and Koton and their coworkers[45] obtained from methacrylic anhydride an 80% yield of a cyclic polymer of high molecular weight, soluble in dimethylformamide, melting at 200°, and of intrinsic viscosity 0.6–0.8. Polymethacrylic acid gave the same product when heated:

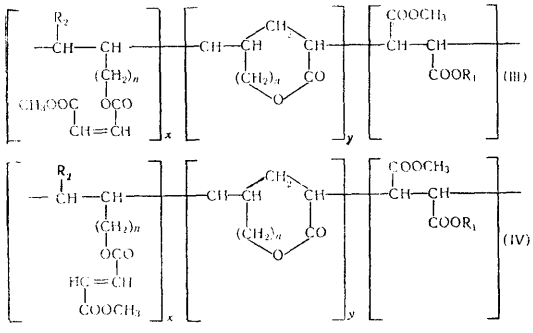


Soluble polymers from unsymmetrical 1,6-dienes are well known. Allyl acrylate is polymerised in dilute solution by benzoyl peroxide[46], allyl methacrylate by benzoyl peroxide on ultra-violet irradiation at 350–380 mμ [47,48], and α-, β-, and γ-methylallyl methacrylates by benzoyl peroxide in toluene[49]. The authors did not propose cyclic structures for the polymers. Butler et al.[50] polymerised pure methyl allyl, methyl but-2-enyl, and methyl but-3-enyl maleates and fumarates by means of benzoyl peroxide (without solvent), obtaining readily soluble linear polymers of low molecular weight and considerable unsaturation (37–77%). The authors suggested structural units derived from γ-butyrolactone, δ-valerolactone, and

ϵ-caprolactone:

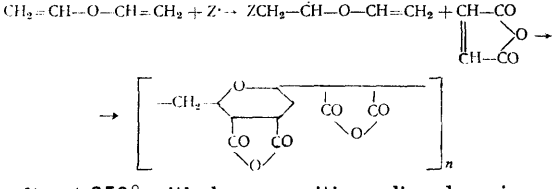


Possible units derived from the maleates (III) and the fumarates (IV) are:

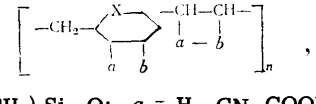


The authors[50] consider that unsymmetrical dienes form cyclic polymers to a lesser degree than do symmetrical dienes. The extent of cyclisation for the six unsymmetrical monomers studied varied from 23% to 60%, compared with complex-cyclisation of symmetrical monomers capable of forming six-membered rings.

Butler[14] studied the copolymerisation of 1,4-dienes with olefines, the mechanism of which is very similar to that described above. Divinyl ether and maleic anhydride copolymerise by a radical mechanism to a linear polyanhydride:

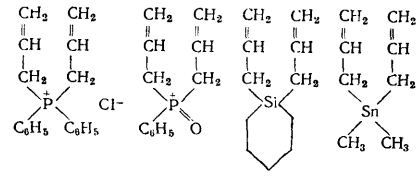


This melts at 350° with decomposition, dissolves in acetone and dimethylformamide, has intrinsic viscosity 0.175 in dimethylformamide, is only slightly unsaturated, and undergoes the usual reactions of anhydrides. Other 1,4-dienes used were divinyldimethylsilane, divinyl sulphone, and divinylcyclopentamethylenesilane; other olefines were fumaronitrile, fumaryl chloride, dimethyl fumarate, diethyl maleate, and vinyl acetate. The copolymers were linear and saturated, the author proposing the structure:

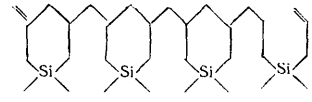


where X = CH_2, $(CH_3)_2Si$, O; *a* = H, CN, COOR; *b* = CN, COOR; *a* - *b* = CO–O–CO.

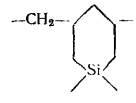
Butler and his coworkers[21] obtained soluble cyclic polymers of low unsaturation, in the presence of radicals or Ziegler catalysts, from the following unconjugated dienes:



Kolesnikov and his coworkers[51] attempted to polymerise diallyldialkylsilanes, the structural analogues of 4,4-dialkylhepta-1,6-dienes. Triethylaluminium and titanium tetrachloride in a non-polar solvent converted diallyldiethylsilane to a soluble polymer of low molecular weight and little residual unsaturation, for which was proposed the tetrameric structure:



Topchiev and his coworkers[52] obtained polymers of unknown structure, mainly liquids, from diallyldimethylsilane and diallylmethylphenylsilane in the presence of a Ziegler catalyst. Bogomol'nii[53] polymerised diallyldiphenylsilane and diallyldimethylsilane with a Ziegler catalyst at 70°–80°, obtaining from the latter a rubber-like polymer soluble to the extent of 80% in benzene, and of intrinsic viscosity 0.05–0.09 in that solvent. Some 20–25% of the units contained a double bond; the author considered the predominant unit to be



Mikulasova and Hrivik[54] showed that diallyldimethylsilane yields a cyclic polymer in the presence of t-butyl peroxide. Marvel and his coworkers[21] have stated that a cyclic polymer of relatively high molecular weight is produced by a Ziegler catalyst from diallyldimethylsilane.

Research into cyclopolymerisation is continuously increasing. Some of these new and unusual polymers, with alternating cyclic and linear segments, will certainly be of practical value.

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Institute of Organometallic Chemistry;
Academy of sciences of the USSR.

OCCURRENCE OF THE TRANSURANIUM ELEMENTS IN NATURE

R. Tsaletka and A. V. Lapitskii

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INTRODUCTION

Whether uranium, with an atomic number of 92, is last in the series of elements or whether elements heavier than uranium can exist, is a question that has interested chemists ever since the discovery of the Periodic Law. The correct answer to this question could only be given by contemporary chemists and physicists when heavy elements lying beyond uranium in the Periodic Table were produced artificially in 1940. Mendeleev himself admitted the possibility of extending the Periodic System to include elements heavier than uranium. Later, a great deal of work was devoted to the investigation of the possible existence of transuranium elements and to the structure of their electron shells.

Attempts to detect transuranium elements in nature have been made for some time. Reports have repeatedly appeared in the literature concerning their natural occurrence but, after more careful study, these data have mostly proved to be incorrect. The chief reasons for the lack of success were: (1) unreliable methods of investigation; (2) wrong placing of the transuranium elements in the Periodic Table, whereby they would constitute a group of analogues to osmium, iridium, and platinum, i.e. element 93 should be the analogue of manganese and rhenium, element 94, of ruthenium and osmium, and so on. On this hypothesis, Loring and Druce[1-4] undertook a search for element 93 in samples of manganese and rhenium using X-ray analysis. They discovered weak lines in the wave-length region predicted for this element. They considered this as proof (though not conclusive) of the presence of element 93 in manganese ores. It was established later that the observed lines belonged to other elements.

In 1934 Koblic reported[5] that he had discovered element 93, for which he proposed the name "bohemium", in