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POLYMERISATION OF ISOBUTENE

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INTRODUCTION

As is well known, much attention is now being paid to development of the chemical industry in this country, and in particular to production of high polymers, plastics, synthetic rubbers, and fibres. Products from the processing of gas and petroleum must form the basic raw materials for this new growth of the chemical industry.

In recent years processes for polymerising and copolymerising unsaturated compounds, particularly alkenes (ethylene, its homologues, and derivatives), have become important. The study of alkene polymerisation is based on the work of Russian and Soviet chemists, in the first place that of A. M. Butlerov. Both in the USSR and elsewhere the industrial utilisation of alkene-polymerisation processes for industrial gases has been under investigation for some decades; useful catalysts have been sought and prepared, and reaction mechanisms studied. It has been found that various acids (sulphuric, phosphoric, and hydrofluoric), natural and artificial aluminosilicates, halides of certain elements (aluminium, boron, zinc, titanium, tin, etc.), and individual metal oxides, are catalysts for polymerising the simplest alkenes to produce liquid products (motor spirits and viscous oils). More recently the polymerisation of alkenes to macromolecular solid polymers (polythene, polypropylene) has acquired great theoretical and practical interest. This can take place at ultra-high pressures in the presence of initiators (oxygen, organic peroxides), and also at atmospheric or elevated pressures in the presence of catalysts (metal oxides, organic aluminium compounds and titanium tetrachloride).

Of the alkene monomers used in industrial polymerisation processes, special interest attaches to isobutene, ethylene, and propene. Isobutene is a relatively accessible substance, which polymerises to a number of valuable products, superior in some respects to similar products obtained from other alkenes. Among these may be mentioned the isomeric isooctenes which are hydrogenated to isooctane (valuable as a petrol additive), high-quality lubricating oils, synthetic rubbers, and plastics.

The present article is a review of literature and patent information on isobutene polymerisation. Catalytic polymerisation of isobutene is of great practical importance and particular attention is given to it.

I. POLYMERISATION OF ISOBUTENE BY HEAT, FREE RADICALS, AND OTHER ACTIVE PARTICLES

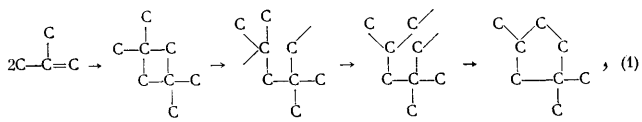
1. Action of Heat

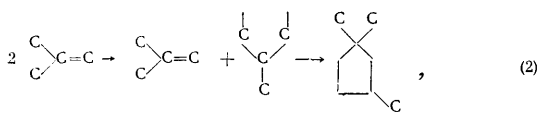
It has been shown that isobutene[1] and t-butanol[2] decompose at dark-red heat, giving complex mixtures of products. According to Ipat'ev[3] polymerisation of isobutene in an iron tube at 380°–390°, with an initial pressure of 70 atm, leads to formation of a mixture of liquid saturated, unsaturated, and naphthenic hydrocarbons.

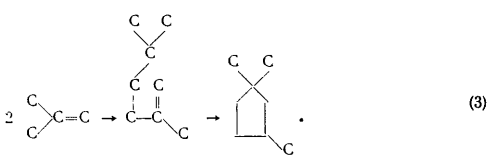
Hurd and Spence[4] considered that thermal activation of C–C and C–H bonds in isobutene leads to formation of univalent radicals, which further change into gaseous products, while activation of the C=C double bond leads to formation of diradicals $(CH_3)_2-\dot{C}-\dot{C}H_2$, giving rise to cyclohexane derivatives and to aromatic hydrocarbons derived from them. Gapon[5] put forward a similar hypothesis of formation of diradicals from alkenes by thermal activation.

According to Lebedev and Koblyanskii[6], when liquid isobutene was heated at 200° and 30 atm in a carbon dioxide atmosphere in sealed refractory glass tubes for 14 days, 6–8% of it polymerised, exclusively to triisobutene. Thermal polymerisation of isobutene in sealed tubes at ~370° is a homogeneous second-order reaction[7] with an activation energy of 43 kcal/mole.

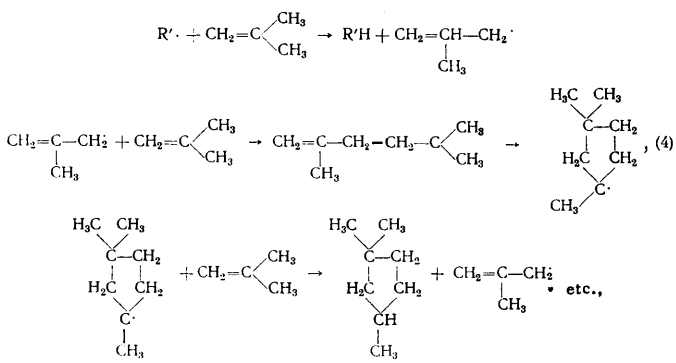
At 370°–460° and 36–360 atm isobutene[8] undergoes cyclodimerisation, the reaction-product (1,1,3-trimethylcyclopentane) yield being raised by increasing the time of heating or the highest pressure attained. A heating time of 1 h at 400°, pressure 36 atm, gave a liquid polymer with the highest content of dimer (49.5%). The gaseous reaction products, comprising ~4 wt.% of the reacted isobutene, contained isobutane, propane, propene, and traces of methane, in addition to isobutene. 1,1,3-trimethylcyclopentane was also obtained by thermal dimerisation of isobutene using a diluent (nitrogen)[9]. It has been suggested[8] that cyclodimerisation can take place by one of the following routes:


(1)


(2)


(3)

The last reaction scheme is the most probable one; it involves a radical chain mechanism, and can be depicted thus:


(4)

Stepukhovich and Mitenkov[11] described an interesting case of thermal polymerisation of isobutene. They studied its low pressure cracking at 811°–828°K and 2 mm Hg, when, instead of a pressure increase due to isobutene decomposition, there was an appreciable pressure drop (up to 20%). Apparently there was absorption of molecules of isobutene on the walls of the quartz reactor, and then heterogeneous catalytic polymerisation of isobutene took place at those parts of the walls covered by the absorbed molecules, polymerisation at first prevailing over cracking.

2. Action of α-Particles

Polymerisation of isobutene by α-particles has been little studied. Mund and coworker[12,13] found that this process has a negative temperature coefficient. The reaction rate can be represented by the semi-empirical equation

$$1/P = 1/P_0 + k(1-e^{-\lambda t}) - k'(1-e^{-at-bt^2}), \quad (6)^*$$

where P_0 is the initial pressure, P the pressure at time t, λ the radioactive (decay) constant for radon (0.0075), and a, b, k, and k' are constants. At 0° and 31°, 22 and 55 molecules respectively of isobutene were polymerised per ion. The authors ascribed the rapid drop in polymerisation rate with rise in temperature, not to change in the number of chains, but to change in their length. A small amount of hydrogen was formed, and the mean molecular weight of the polymer was ~4000. When isobutene was polymerised by α-particles at constant pressure (400–700 mm Hg at 0°), the ion yield was 33.6–46.2, and the mean molecular weight of the resultant polymer was 400–700.[14] The authors believed that the first stage of the process proceeds as follows:

$$\begin{aligned} &1)\ C_4H_8 \xrightarrow{\alpha\text{-particle}} C_4H_8^+ + e, \\ &2)\ C_4H_8^+ + e \rightarrow C_4H_7^{\cdot} + H, \\ &3)\ H + C_4H_8 \rightarrow C_4H_7^{\cdot} + H_2. \end{aligned} \quad (7)$$

3. Action of Radicals Formed by Photolysis of Aldehydes and Ketones

The rate of photolysis of the simplest aldehydes and ketones at 300° is decreased by admixture with alkenes[15]. Under these conditions the alkene is polymerised by each light quantum absorbed by the carbonyl compound, and the rate of polymerisation is independent of alkene pressure. Polymers of low molecular weight are formed, isobutene giving a dimer. The equations for the process are:

$$\begin{aligned} &CH_3CHO + h\nu = CH_3 + CHO, \\ &CH_3 + CH_3CHO = CH_3 + CH_4 + CO, \\ &CH_3 + CH_3 = C_2H_6, \\ &CH_3 + C_nH_{2n} = R_1, \\ &R_1 + C_nH_{2n} = R_2, \\ &R_{n-1} + C_nH_{2n} = R_n. \end{aligned} \quad (8)$$

It was assumed that chain breaking was due to isomerisation of a large radical into a species of low reactivity.

4. Electric Discharges

Electric discharges act on alkenes, and more specifically, on isobutene, in various ways, depending on the nature of the discharge. An arc discharge, like high temperatures, causes profound decomposition of isobutene

* Eqn. (5) is missing from Russian text (Ed. of Translation).

molecules, while the silent discharge brings about polymerisation[16], as first observed by Dem'yanov and Pryanishnikov[17]. The experiments were carried out in an ozoniser, in which a discharge occurred at various alternating currents, the potential difference being 12–13 kV. A yellowish oil was obtained, average molecular weight 140, consisting mainly of diisobutenes and triisobutenes, but containing a small amount of a hydrocarbon C_5H_8. The authors[17] advanced a hypothesis that the silent discharge not only opens the alkene double bond, leading to polymerisation, but also splits off radicals. Pryanishnikov[18] made a more detailed investigation of polymerisation of isobutene by the silent electric discharge. The light fractions of the liquid polymerisation product contained 70–80% of saturated and 20–30% of unsaturated hydrocarbons, while in the high-boiling fractions the ratio was reversed (40 : 60). Polymerisation was accompanied by splitting off and addition of radicals, as was shown by the presence of C_6 and C_7 hydrocarbons (2,2-dimethylbutane and 2,2-dimethylbutene, 2,4- and 2,2-dimethylpentanes, and 2,2,3--trimethyl butane and the corresponding alkenes). Naphthenes were also present in the high-boiling fractions. Isomura[19] observed the formation of a liquid product of mean molecular weight 152 and consisting mainly of three fractions: 80°–85°, 100°–110°, and 190°–200°. Otto and Müller-Cunradi[20] obtained lubricating-oil additives by polymerising isobutene in the silent electric discharge.

5. Action of Peroxides and Other Substances Giving Free Radicals

Little attention has been paid to the polymerisation of isobutene in the presence of substances which can decompose to give free radicals. The existing patent literature describes mainly processes for copolymerising isobutene with other unsaturated compounds to obtain macromolecular substances of the synthetic-rubber type. Among the substances which have been copolymerised with isobutene are alkenes, alkadienes, styrene[21], aldehydes, and ketones having an α-hydrogen atom[22,23], and C_2F_4.[24] The following can be used as initiators: benzoyl peroxide[22]; dialkyl peroxides[25]; organic polyperoxides[26]; hexachloroethane, $(NH_4)_2S_2O_8$; $N_2H_4 \cdot 2HCl$, $NH_2OH \cdot HCl$[23]; $R_3C(CR_2)_nR$, where R can be phenyl or substituted phenyl but not hydrogen[21,27]; imino compounds of the type $RR'C{=}NA$, where R and R' are hydrogen or hydrocarbon radicals, and A is H, OH, NH_2, or $N{=}CR''R'''$; nitro derivatives of hydrocarbons[28]; and also substances giving diradicals on homolysis[29]. Copolymerisation takes place over a wide temperature range (-164° to 550°, depending on the initiator used), and at pressures up to 3000 atm.

Polymerisation is sometimes carried out in emulsions using peroxide catalysts plus emulsifiers. It then takes place at much lower temperatures and is characterised by a higher reaction rate. The literature does not describe polymerisation of pure isobutene in aqueous emulsion. Usually it is copolymerised with other unsaturated compounds, e.g. fumaric esters[30-32], acrylonitrile, methyl methacrylate, vinyl acetate, unsymmetrical dichloroethylene, methyl chloroacrylate, styrene[33], and vinyl halides[33,34]. The aqueous emulsion must have pH 3–8.5. The process is carried out at 50°–100° in the presence of potassium persulphate, H_2O_2, and similar materials[30], with added emulsifiers, usually sodium or potassium stearate.

Isobutene has also been copolymerised with acrynonitrile in suspension in a medium in which only the initiator, and not the starting materials or final product, was soluble. The mixtures contained up to 85% of acrylonitrile[35].

II. CATALYTIC POLYMERISATION OF ISOBUTENE

1. Acid-Catalysed Polymerisation

Sulphuric acid. Butlerov and Goryainov[36,37] first described the polymerisation of isobutene by sulphuric acid. When isobutene was absorbed in sulphuric acid ($H_2SO_4 : H_2O = 3 : 1$) a quantity of oil always accompanied the t-butanol formed. Half of this oil was triisobutene, but it also contained a small amount of higher polymers. When isobutene was passed into strong sulphuric acid, it was all converted to triisobutene plus higher polymers[38]. Dimerisation was observed with much diluted acid[39].

Diisobutene is obtained by dissolving 1 volume of liquid isobutene in 2 volumes of concentrated H_2SO_4 which has been diluted with an equal volume of water, and then heating in sealed tubes to 100°. Diisobutene can also readily be obtained by heating a mixture of dilute H_2SO_4 and t-butanol[38]. According to Butlerov[40], isobutene cannot be dimerised directly to diisobutene, but only through t-butanol as an intermediate, the latter forming diisobutene when heated at 100° with dilute H_2SO_4. At ordinary temperature, without the hydration stage, the trimer immediately results, and when concentrated H_2SO_4 is used, higher polymers are also obtained.

By passing isobutene through aqueous sulphuric acid (5 : 1), Lebedev and Koblyanskii[6] obtained a product containing 1% diisobutene, 90% triisobutene, and 9% polyisobutenes. Butlerov's trimer contained two isomers: 90% of a low-boiling one and 10% of a high-boiling one.

In the copolymerisation of isobutene with n-butenes in the presence of sulphuric acid to obtain isooctane[41], 60–75% H_2SO_4 selectively absorbs isobutene in the cold. A temperature of 20°–40° is required to obtain an appreciable increase in polymerisation rate. Raising the temperature to 100° doubles the polymer yield. The dimer is the main product when isobutene alone is polymerised by 70% sulphuric acid at 20°.

Katsuno[42] showed that if the sulphuric acid concentration is below 77%, the isobutene polymerisation product consists mainly of dimer and trimer. Lowering the acid concentration and raising the temperature raises the yield of dimer. With 58% H_2SO_4 at 68°–71° the dimer yield was a maximum (70%). The dilute acid absorbs isobutene slowly. Higher acid concentration and lower temperature favour a higher degree of polymerisation.

Isobutene was rapidly absorbed by 77% H_2SO_4 at room temperature, to give a 70% yield of trimer consisting of 2,2,4,6,6-pentamethylhept-3-ene, 2,2-dimethyl-4-neopentylpent-3-ene, and 2,2-dimethyl-4-neopentylpent-4-ene, in the ratios 1 : 2 : 1*. When the temperature was lowered below 20°, 67% sulphuric acid did not cause polymerisation, but there was absorption with formation of t-butanol. However, when this mixture was kept at 70°–100°, polymerisation occurred, and part of the isobutene was regenerated. By previously diluting the mixture with water,

* This account follows Chem. Abs., 43, 5176 (1949) (ref. 42), but 2,2-dimethyl-4-neopentylpent-3-ene is the same as 2,2,4,6,6-pentamethylhept-3-ene (Ed. of Translation).

the rate of polymerisation could be lowered and the yield of dimer raised. The product of slow polymerisation at room temperature was mainly trimer. The di- and triisobutenes formed can undergo secondary changes in the presence of sulphuric acid.

The polymerisation of isobutene is reversible, and low temperatures favour shift of equilibrium in the direction of polymer formation. At 100° equilibrium is shifted towards the trimer. The temperature for polymerisation of isobutene by H_2SO_4 can be lowered to 0° [43], but then the acid concentration must not be less than 85–90%. At 0° there is 85% conversion of isobutene to liquid polymers.

According to Nametkin[44], the polymerisation of alkenes by concentrated sulphuric acid, gives both unsaturated polymers and also saturated hydropolymers; the appearance of the latter implies that hydrocarbons more unsaturated than the alkenes are formed. This process, called hydro-dehydropolymerisation, occurs readily with isobutene, a series of hydropolymers being formed, from hydrodimer to hydrohexamer and higher:

$$\begin{gathered} H_2SO_4 + C_4H_8 \longrightarrow HOSO_2OC_4H_9 \xrightarrow{C_4H_8} H_2SO_4 + C_8H_{16}, \\ C_8H_{16} + C_4H_9OSO_2OH \longrightarrow C_8H_{18} + HOSO_2OC_4H_7, \\ nC_4H_7OSO_2OH \longrightarrow (C_4H_6)_n + nH_2SO_4. \end{gathered} \quad (9)^*$$

Many workers[38,45-53] have investigated the structures of the isobutene polymers formed by the action of sulphuric acid. It has been found that the dimer consists of 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene in the ratio of 4 : 1.

Investigation of the trimeric fraction of the isobutene polymers[40,54-59] showed that it contained 2,2,4,6,6-pentamethylhept-3-ene, 4,4-dimethyl-2-neopentylpent-1-ene, 2,4,4,6,6-pentamethylhept-1-ene, and 2,4,4,6,6-pentamethylhept-2-ene.

In the light of the results obtained[59] the following reactions can be postulated. A proton, H^+, plus an isobutene molecule form a carbonium ion:

$$(CH_3)_2C{=}CH_2 + H^+ \rightleftarrows \underset{(I)}{(CH_3)_3C^+}. \quad (12)$$

The carbonium ion (I), like a proton, adds to an isobutene molecule giving the carbonium ion (II):

$$(CH_3)_3C^+ + CH_2{=}C(CH_3)_2 \rightleftarrows \underset{(II)}{(CH_3)_3CCH_2C^+(CH_3)_2}, \quad (13)$$

which can, with loss of H^+ from the methylene group or from a methyl group, give the two isomers of diisobutene:

$$(CH_3)_3CCH_2C^+(CH_3)_2 \nearrow (CH_3)_3CCH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CH_2 + H^+ \quad \searrow (CH_3)_3CCH{=}C(CH_3)_2 + H^+. \quad (14)$$

The formation of mainly 2,4,4-trimethylpent-1-ene can be explained by the proton splitting off more readily from a methyl group attached to the electron-deficient carbon atom, than from the neopentyl group.

When diisobutene adds H^+, it gives the carbonium ion (II). Similarly it can add the carbonium ion (I). But addition of (I) to β-diisobutene does not occur, since formation of 2,4,4-trimethyl-3-t-butylpent-2-ene has not been observed. The union of (I) with α-diisobutene can be depicted thus:

$$(CH_3)_3C^+ + CH_2{=}C(CH_3)CH_2C(CH_3)_3 \rightleftarrows \underset{(III)}{(CH_3)_3CCH_2C^+(CH_3)CH_2C(CH_3)_3}. \quad (15)$$

(III) splits off a proton, either from the adjacent methylene group or from a methyl group:

$$(III) \nearrow (CH_3)_3CCH_2{-}\underset{\displaystyle CH_2}{\overset{\displaystyle \|}{C}}CH_2C(CH_3)_3 + H^+ \ (54\%) \quad \searrow (CH_3)_3CCH{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}CH_2C(CH_3)_3 + H^+ \ (36\%). \quad (16)$$

The ion (II) can also add to isobutene:

$$(CH_3)_3CCH_2C^+(CH_3)_2 + CH_2{=}C(CH_3)_2 \rightleftarrows \underset{(IV)}{(CH_3)_3CCH_2C(CH_3)_2CH_2C^+(CH_3)_2}. \quad (17)$$

The ion (IV), losing a proton, gives the trimers:

$$(IV) \nearrow (CH_3)_3CCH_2C(CH_3)_2CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CH_2 + H^+ \quad \searrow (CH_3)_3CCH_2C(CH_3)_2CH{=}C(CH_3)_2 + H^+ \Big\} 10\% \quad (18)$$

Phosphoric acid. Of all acids, phosphoric acid and its salts are the most widely used for alkene polymerisation. The acid is usually employed in the liquid form, or as the "solid" acid, or as copper pyrophosphate. Sometimes phosphorus pentoxide is used.

When isobutene, n-butenes, or ethylene is slowly passed over P_2O_5 spread on pumice, there is complete gas absorption at room temperature, after an induction period of a few hours[60]. When the catalyst saturated with gas is heated to 110°, pure dimerised isobutene boils off. With a reaction temperature above 110°, trimer and tetramer are found in the products.

According to Ipat'ev and Corson[61,62], isobutene at atmospheric pressure is polymerised much faster by liquid orthophosphoric acid than n-butenes, and the presence of isobutene accelerates the polymerisation of but-1-ene. Mixtures of isobutene and n-butenes polymerise at lower temperatures and at lower acid concentrations than the n-butenes alone, a mixture of alkenes being formed.

Mild polymerisation conditions favour formation of the simpler polymerisation products, e.g. the isobutene polymers formed at 30° contained only two components, diisobutene and triisobutene, whereas the polymers formed at 130° contained seven compounds. 100% orthophosphoric acid is a more powerful polymerisation catalyst than the 95%, 89%, and 85% acids; pyrophosphoric acid on pumice[63] is more active than metaphosphoric acid.

A comparative study of the polymerisation of isobutene by sulphuric and orthophosphoric acids showed[64] that at 110° and atmospheric pressure the concentration of H_2SO_4 must not exceed 65%; if it does, profound decomposition of the reaction product is observed. Under the same conditions 87–100% orthophosphoric acid was more active, and the activity was enhanced by addition of 4–5% H_2SO_4. Addition of over 10% H_2SO_4 favoured decomposition of the reaction products.

With pumice impregnated with 87–100% H_3PO_4, isobutene at 30°–150° was converted to a product comprising 55–60% of dimer and 25–30% of trimer. When the temperature was raised above 30°, the rate of polymerisation first increased, passed through a maximum, and then, because of depolymerisation, fell. With 87% H_3PO_4 the optimum temperature was 110°, and for 100% acid it was 130°.

With P_2O_5 on pumice the contraction of the gas was very great at the beginning of reaction, then it rapidly decreased, and afterwards became steady. When the temperature was

* Eqns. (10) and (11) are missing from the Russian text (Ed. of Translation).

raised, the contraction diminished, but this happened at lower temperatures than with H_3PO_4 on pumice.

One catalyst, active charcoal containing up to 76% H_3PO_4, was 5–6 times as active for polymerising isobutane at 50°–55° as liquid orthophosphoric acid[65]. When reaction was effected with a layer of catalyst (4–5 mm), the polymers contained up to 53% of dimeric material. Decreasing contact time decreased the formation of high polymers, but did not affect the yield of trimeric isobutene.

The acid phosphate of iron, $Fe(H_2PO_4)_3$, deposited on charcoal, caused (in a 10 mm layer) reaction at 50°–60° under a pressure of 10–30 atm[66]. Reaction took place to the extent of 5–7%, dimer being formed. The catalyst was unstable because of hydrolysis of the salt and leaching out of the acid. A more stable catalyst, $Fe(H_2PO_4)_3 \cdot 2H_2O$, contained excess phosphoric acid and gave a product containing up to 80% of dimer. Raising the temperature to 105°–110° led mainly to the formation of trimers. Moisture in the starting material, while increasing the rate of polymerisation, particularly at 100°–105°, decreased the amount of dimer in the polymers and caused a rapid fall in catalyst activity. A catalyst of composition $FeH_3(PO_4)_2 \cdot 2.5H_2O$ was somewhat less active than the one just described, and gave up to 66% of dimer.

Hydrogen fluoride. Polymerisation of isobutene by hydrogen fluoride[67–69] takes place at ordinary or enhanced temperature under slight pressure. But side reactions leading to fluorination and destruction of the polymers also occur, particularly at elevated temperatures.

Fluorophosphoric acids. Topchiev and Andronov[70] showed that mono- and difluorophosphoric acids and their molecular compounds with BF_3 can be active catalysts for polymerising isobutene. Silica gel and activated carbon were used as supports for them. The nature of the support and the contact time had a considerable effect on the extent of polymerisation.

Polymerisation took place at 15°–152° and atmospheric pressure. As the temperature was raised, the degree of polymerisation fell and the yields of dimeric and trimeric fractions rose. Higher temperatures favoured isomerisation; in addition to 2,4,4-trimethylpent-1-ene and -2-ene, the dimer contained isomeric octenes, such as 2,3,4-trimethylpent-2-ene. When silica gel was used, the polymers were more volatile than with carbon, but the polymer yield was considerably less. The carbon-supported catalyst was the more stable. The order of catalytic activity was:

$$HPO_3 \cdot BF_3 > H_3PO_4 \cdot BF_3 > HPO_2F_2 > H_2PO_3F.$$

Dihydroxyfluoroboric acid. This was used[71] as a catalyst for copolymerising isobutene with propene or n-butenes at 0°–40° and 3–8 atm. The polymers were hydrogenated; the product from isobutene and propene contained 67% of heptanes, 95% being 2,3-dimethylpentane. The yield of the C_8 fraction from hydrogenated isobutene–but-1-ene copolymer was ~43%, and it contained 34% of dimethylhexanes and 66% of trimethylpentanes. In the same way the yield of the C_8 fraction from hydrogenated isobutene–but-2-ene copolymer was 36%, and it consisted wholly of trimethylpentanes.

Sulphonic Acids. C_1–C_4 sulphonic acids are effective catalysts above 60°. At lower temperatures they react with alkenes to give stable esters[72]. Polymerisation can be carried out in two ways: (1) by preparing the ester and then heating it at 60°–120° with free acid, in which case there is an induction period of up to 60 min; (2) by passing the alkene at atmospheric pressure into the acid heated to a temperature high enough for polymerisation to take place without intermediate formation of esters. Isobutene is readily polymerised even at room temperature, trimer being the main product.

The patent literature mentions trichloroacetic acid and hexanoic acid[73] as isobutene polymerisation catalysts.

The following conclusions can be drawn from this review of the acid polymerisation of isobutene and from the amounts and structures of the polymers formed: Isobutene is usually acid-polymerised at 0°–300°, and as the temperature is raised side reactions are accelerated. For example, with H_3PO_4 the products of polymerisation at 100° are just polymers; at 100°–300° depolymerisation products accompany the polymers, while above 300° saturated and naphthenic hydrocarbons are formed.

With sulphuric acid, the temperature range for forming solely polymers of the starting alkene is much less, but it is hard to define it precisely, since not only temperature, but also the acid concentration and the pressure have great influence on isobutene polymerisation.

When hydrofluoric acid is used as catalyst, it brings about polymerisation of the isobutene accompanied by formation of products of various molecular weights which are not actually polymers.

The mechanism of acid polymerisation, with particular reference to ethylene and propene, has been discussed in a paper[75] to which one of the present authors contributed. The schemes to which most attention should be paid are those involving intermediate formation of esters[61,62] and one which involves assumed C–C or C–H scission giving rise to a methyl group plus an alkene radical or to a hydrogen atom plus an alkene radical, which initiate polymerisation by adding to the alkene double bond[76]. Lately, however, a scheme put forward by Whitmore[77] (and discussed above), involving carbonium ions, has gained widespread acceptance. Many authors have discussed this mechanism in detail; among other things it is assumed that polymerisation involving carbonium ions is a chain reaction[10,74,78].

2. Halide-Catalysed Polymerisation

Metal halides. The course of polymerisation of the lower alkenes — in particular isobutene — by metal halides depends to a considerable extent on the reaction temperature. At 0°–200° liquid products are usually formed, consisting mainly of dimers and trimers of the starting alkene. At -80° to -160° the so-called low temperature polymerisation of alkenes occurs; it is of great practical importance because it results in high-molecular-weight polymers[79]. This process, brought about by catalysts of the Gustavson–Friedel–Crafts type, usually takes place in the liquid phase with a diluent which is either inert or else forms a complex with the catalyst. The amount of catalyst is usually ~0.1% of the isobutene. Low temperature polymerisation of isobutene[80,81] is a chain reaction and takes place with almost explosive speed. Rubber-like solid polymers of molecular weight over 100 000 can be obtained in quantitative yields.

The molecular weight of the polymer increases when the temperature is lowered from -20° to -100°. Thus when isobutene is polymerised at its boiling point an oily polymer is formed after a considerable induction period, but

at -80° a solid polymer is formed without any induction period.

Addition of other alkenes, e.g. n-butenes, to the isobutane lowers the yield and the molecular weight of the polyisobutene; this reduction is very marked when diisobutene or triisobutene are added. This shows that though polymerisation must proceed in successive stages, the dimer and trimer are not intermediates, a view which is further supported by the fact that di- and triisobutenes, which undergo slow polymerisation to oils at room temperature, do not give macromolecular products at low temperatures.

Alcohols and ethers, e.g. diethyl ether[82], have, like alkenes and alkadienes, a retarding effect on the reaction.

Beryllium halides. Polymerisation of isobutene in the presence of $BeCl_2$,[83,84] at 200° and initial pressure 27 atm, affords an 80% yield of hydrocarbons; 80% of the liquid hydrocarbons are a benzine fraction comprising mainly diisobutene and isomeric hydrocarbons plus triisobutene and its isomers. A tetramer occurs in the high-boiling fraction, and in the low-boiling material there are isopentane, isohexane, and isohexene. The gaseous products are: propene, n-butenes, and unchanged isobutene.

When reaction is carried out using $BeCl_2$ in sealed glass tubes, more than half of the polymerisate is a viscous oil. The difference in the way in which reaction takes place indicates additional catalysis by the walls of the reactor. BeF_2 is a less active catalyst than $BeCl_2$.

Zinc chloride. The tendency of isobutene to be polymerised by $ZnCl_2$ at room temperature has long been known. According to Kondakov[85], reaction of isobutene with zinc chloride in sealed tubes gave a solid crystalline product and a liquid mixture consisting of diisobutene and t-butyl chloride, taken to be an intermediate reaction product. Polymerisation of isobutene at room temperature took place relatively slowly, the main reaction products being diisobutene, octyl chloride, and an insignificant quantity of trimer. The reaction rate increased appreciably when the temperature was raised or the amount of zinc chloride was increased, di-, tri-, and tetraisobutenes being obtained. The resultant polymers were identical with the polymers obtained by Butlerov's method employing sulphuric acid.

Even prior to Kondakov, it was shown[86,87] that isobutanol is changed into a mixture of polyisobutenes (mainly di- and triisobutenes) under the influence of zinc chloride. Addition of HCl accelerates the reaction, which becomes almost explosive: a violent evolution of gas, consisting mainly of isobutene and isobutane, occurs. Petrov et al.[88] investigated the conversion of isobutanol to polyisobutenes at 300°–330°, both at atmospheric pressure and at elevated pressure, and showed that under pressure the yield of diisobutene could be doubled and the catalyst consumption diminished 12-fold. The authors also showed that 2,2,4- and 2,2,3-trimethylpentenes were present in the dimeric material.

Isobutene is not polymerised by $ZnCl_2$ in a copper tube at 600°.[89]

Zinc chloride can be used as a catalyst for copolymerisating isobutene with alkadienes to obtain solid polymers[90].

Boron fluoride and its derivatives. Butlerov and Goryainov[37] reported that alkenes could polymerise in the presence of BF_3. Topchiev and coworkers[91] made a detailed investigation of the polymerisation of isobutene by BF_3 and its derivatives; it was 90–95% polymerised in the liquid or vapour phase in the presence of 1–2% of boron trifluoride etherate deposited on a solid carrier, to give a product containing 20–26% of dimer, 65–75% of trimer, and quite a small amount of higher polymers[91]. The nature of the carrier (activated charcoal, pumice, silica gel, aluminium oxide, and copper turnings), and the temperature over the range 5°–130° did not affect the polymer yield or the ratio of dimer to trimer. Vapour-phase polymerisation of isobutene occurred most effectively at 5°, since at that temperature there was not such extensive loss of catalyst from the carrier as at higher temperatures. The structures of the dimer and trimer were elucidated, and a small amount of saturated hydrocarbon (which could have arisen through hydropolymerisation) was established[92].

The reaction of isobutene in the presence of BF_3 on platinum and on Cr_2O_3 catalysts at various temperatures has been studied in detail[93]. The catalysts used were platinum on activated carbon (Pt + C), Pt + C + BF_3, C + + BF_3, BF_3 + $Cr_2O_3 . Al_2O_3$, and $Cr_2O_3 . Al_2O_3$, at 250°–400° i.e. at temperatures considerably higher than those usually employed in polymerisation of alkenes by BF_3.[94]

With all these catalysts the degree of polymerisation and molecular weights of the products fall with increase in temperature, although the alkene conversion remains rather high. Platinum on carbon alone does not bring about polymerisation of isobutene; with Pt + C + BF_3 the conversion is 90%, and with C + BF_3 it is 65%. At 400° there was also hydropolymerisation and partial aromatisation.

Paushkin and Shcherbakova[95] investigated how the carrier affects the catalytic action of BF_3. Activated carbon and aluminosilicate, both with a 15–20% content of BF_3, were used as catalysts. The nature of the polymerisation both at room temperature and at 100°, as well as the effectiveness of the catalyst, depended on the carrier, though neither activated carbon nor aluminosilicate caused polymerisation of alkenes under the conditions employed.

Activated charcoal plus BF_3 brought about more profound polymerisation than aluminosilicate plus BF_3, or $Et_2O . BF_3$. This was ascribed to a difference in the mechanism of catalysis; in the case of BF_3 plus aluminosilicate, this is similar to the action of BF_3 plus phosphoric acid or BF_3 plus water, and is related to formation of more effective complex acids.

Topchiev and Alyavdina[96,97] showed that the molecular compounds of BF_3 with K_2SO_4 and Na_2SO_4 could be used to polymerise isobutene. When either the reaction temperature or the space velocity was raised, the degree of polymerisation fell. Similar behaviour was observed when silica gel + BF_3 was used as the catalyst, but at 150°, part of the BF_3 was lost from the silica gel surface. The dimeric portion of the polymerisate contained 2,4,4-trimethylpent-1-ene and -2-ene, as well as 3,4,4-trimethylpent-2-ene, and 2,3,4-trimethylpent-1-ene and -2-ene, which shows that isomerisation also takes place.

It is believed that the molecular compound of BF_3 with K_2SO_4 or Na_2SO_4 dissociates at high temperatures,

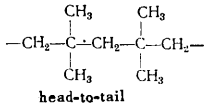
$$K_2SO_4 \cdot BF_3 \rightleftarrows K_2SO_4 + BF_3, \qquad (19)$$

and that the BF_3 liberated brings about the isobutene polymerisation.

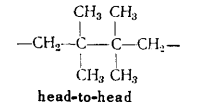
Evans, Polanyi, and coworkers[98] concluded that some third component must be present for rapid low temperature

polymerisation of isobutene in the presence of BF_3. When BF_3 was passed into unpurified isobutene polymerisation occurred very rapidly, but with carefully purified isobutene there was practically no polymerisation. It was concluded that this third component might be water, and support for this view was found when the reaction was carried out in the gas phase in a high vacuum[99]. The polymerisation took place only with impure isobutene containing water, and when the isobutene pressure exceeded a certain value. Purified isobutene polymerised rapidly if it was previously mixed with water vapour: 10^{-1} mm of water vapour was enough to initiate reaction. In addition to water, other effective initiators were t-butanol[100,101] and acetic acid[102]. The action of an activator was ascribed to complex formation with BF_3 and donation of a proton to the alkene, to form a carbonium ion, which initiated polymerisation. By introducing a separately-prepared BF_3-acetic acid complex, rapid polymerisation was brought about, and the authors assumed that it occurred on the surface of the crystals of the complex. Diethyl ether also functions as an activator, but is much less effective than t-butanol or acetic acid.

The product of low-temperature polymerisation of isobutene by BF_3 has a high molecular weight. The structure of a polymer molecule can vary according to the way in which the isobutene molecules are linked together:



head-to-tail (20a)

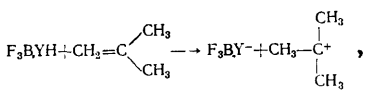


head-to-head (20b)

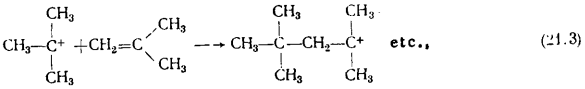
A mixed structure is also possible. Both chemical[81] and physical methods (X-ray analysis[103]) showed that the polyisobutene molecule actually has a head-to-tail structure. However, the authors of the paper referred to thought that the steric hindrance caused by the methyl groups made it necessary to twist successive isobutene units so that the methyl groups of one lay between two methyl groups of another; the molecules thus had a spiral configuration. But if a molecular model of polyisobutene corresponding to (20b) is constructed, no steric hindrance is found, and the molecule is unstrained. We may suppose that with any 1,1-disubstituted ethylene, including isobutene, the heat of formation of a polymer of type (20a) must be abnormally low because of steric hindrance. Calculation of the heat of formation of the hypothetical unstrained head-to-tail polyisobutene by various methods[100,103,104] gives 19.2–24 kcal/mole, which is much above the actual heat of formation of 12.8 kcal/mole[104]. The difference between the heats of formation of hypothetical and actual polyisobutene molecules must be ascribed to steric hindrance being overcome in the actual molecule.

Evans and Polanyi[100] put forward the following scheme for the low-temperature polymerisation of isobutene by BF_3:

$$BF_3+YH \longrightarrow F_3BYH, \qquad (21.1)$$



(21.2)



etc., (21.3)

where YH is a compound containing mobile hydrogen. Stages (21.2) and (21.3) are analogous to the stages of the ionic mechanism advanced for the ordinary acid polymerisation of alkenes[77,105].

The affinity of an alkene molecule for a proton and for a carbonium ion increases on passing from ethylene to isobutene. The affinity is also greater for addition of a proton to the first C atom (methylene group) than it is for addition to the tertiary C atom, in agreement with Markovnikov's rule. Hence the authors[100] conclude that a tertiary carbonium ion will always participate in reaction (21.2). In chain propagation (21.3) the carbonium ion adds on so that the terminal group is always a tertiary one, and in this way the head-to-tail structure comes about. In addition to the ionic mechanism for this reaction, the authors consider the possibility of a radical one.

However, Houtman[106], who investigated the polymerisation of isobutene by BF_3 and $AlCl_3$, came to the conclusion that the presence of moisture, to act as activator, is not essential with these catalysts. A mechanism was advanced in which both π electrons of the alkene are fixed by the catalyst on one of the two carbon atoms joined by the double bond, so that a dipole is formed, and this, adding other monomer molecules, give a macromolecular product. Houtman allows Evans and Polanyi's[100,104] mechanism for formation of low-molecular-weight polymerisation products, but he considers that it is wrong to identify that mechanism with the low-temperature polymerisation one.

Dainton and Sutherland[107] considered that the mechanism for low-molecular-weight polymerisation of isobutene closely resembles that for the macromolecular one. From infra-red spectra, they demonstrated that the products of both reactions have $C(CH_3)_3$ and $-CH_2-C(CH_3)=CH_2$ as end groups, and they uphold the mechanism which Evans and Polanyi previously advanced[100].

Later Evans and coworkers[101,108] again confirmed that the presence of a third component (H_2O, t-butanol, acetic acid, or diethyl ether) is essential for both low- and high-temperature polymerisation of isobutene by BF_3. The third component forms stable complexes, and reaction takes place on the surface of crystals of the complex; in this respect there is no difference between high- and low-temperature polymerisation. Reaction can occur either via a carbonium ion, or via radicals. A carbonium ion is formed by addition of a proton from the catalyst complex to the alkene, and not by addition of the alkene to the catalyst.

But there are facts which indicate that the mechanisms of low- and high-temperature polymerisation of isobutene by BF_3 are not the same. For example, many substances, such as HCl, which facilitate high-temperature polymerisation (as mentioned above), retard low-temperature polymerisation[80,81].

Topchiev et al. showed[80] that the activity order for low-temperature polymerisation of isobutene by various BF_3 compounds in the absence of solvent was

$$BF_3>C_6H_5OCH_3\cdot BF_3>H_2O\cdot BF_3>H_3PO_4\cdot BF_3>(C_2H_5)_2O\cdot BF_3, \qquad (22)$$

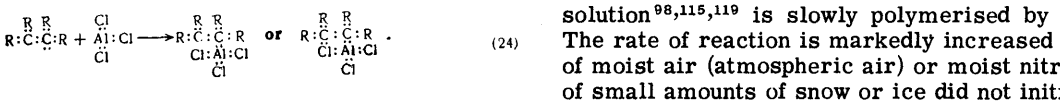
while for high-temperature polymerisation there is a different series[109]:

$$H_3PO_4\cdot BF_3>H_2O\cdot BF_3>H_2SO_4+BF_3>BF_3>RO\cdot BF_3. \qquad (23)$$

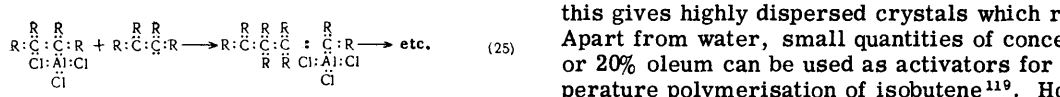
This difference is ascribed to there being different mechanisms for the stepwise polymerisation and the chain polymerisation of isobutene.

Aluminium chloride. Gustavson also used aluminium chloride as a polymerisation catalyst for alkenes[110]. Later[111] the polymerisation of isobutene by $AlCl_3$ at 100° and 150° was studied. A complex of the composition $(AlCl_3 \cdot C_4H_8)_n$ was obtained, together with a liquid polymerisate which contained paraffins and naphthenes in addition to alkenes. Isobutene is polymerised very violently by $AlCl_3$ [105], and reaction begins as soon as the gas comes into contact with the catalyst. Two layers are obtained; the upper one is a colourless oil of average molecular weight 200 and bromine number 10–15, and the lower one, a red viscous oil, is a complex containing 11.5% of aluminium. Further reaction of isobutene with this complex gave a quantitative yield of a colourless oil, and the aluminium content of the complex fell to 8.75%. If the isobutene and complex reacted at 140°, the final complex salt contained 10.5% of aluminium. Treatment of the complex with water afforded a yellowish oil, molecular weight ~270. Isobutene plus ether vapour reacted violently with $AlCl_3$, giving a viscous red oil containing ~12% of aluminium. Isobutene was not polymerised at room temperature or at 140° by the complex $Al_2Cl_6 \cdot 2C_6H_5N(CH_3)_2$, but polymerisation took place with $Al_2Cl_6 \cdot C_6H_5N(CH_3)_2$ and the composition of the complex changed until it became completely inactive, when it contained 10.48% Al and 2.63% N, corresponding to the composition $Al_2Cl_6 \cdot C_6H_5N(CH_3)_2 \cdot 2C_4H_8$.

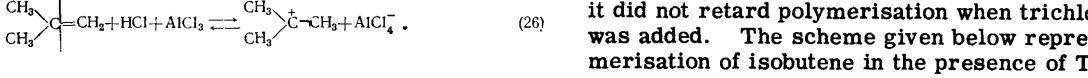
In metal halides of the aluminium chloride type the metal has an incomplete electron octet and can act as an electron acceptor. Aluminium usually has the coordination number 4 in the formation of aluminium chloride complexes, and it can add an electron pair from an active donor, e.g. from an alkene molecule. Polymerisation of alkenes by $AlCl_3$ can be depicted thus[105]:


(24)

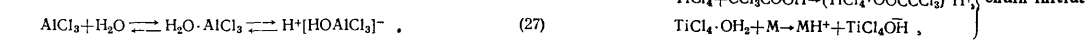
The polymer chain grows by successive addition of an alkene molecule to this complex:


(25)

However, there is reason to doubt whether such compounds are active catalysts for the polymerisation of alkenes. As indicated above, boron trifluoride gains activity by the addition of an activator having mobile hydrogen in its molecule (water, acetic acid, etc.[101,112]). Other metal halides behave similarly in the presence of activators ($SnCl_4$, etc.[113]). So a number of authors assumed[98,99,112-116] that polymerisation of alkenes takes place only by reaction of metal halide with activator present. It is possible that the activator is a source of protons which, adding to the alkene molecule, give a carbonium ion. With aluminium chloride and HCl a carbonium ion can be formed by the reaction[78]


(26)

In the presence of water a proton can be given off by the complex formed from the catalyst and activator:


(27)

This complex is decomposed with formation of HCl, which is a proton source:


(28)

Other schemes have been put forward to explain the catalytic action of systems comprising catalyst and activator, in which the polymerisation is considered to be initiated by energy liberated by addition of activator to catalyst or processes involving hydro- or dehydrohalogenation are postulated. But these mechanisms are less probable than carbonium ion ones[114].

Low-temperature polymerisation of isobutene has been carried out in pentane solution in the presence of $AlCl_3$ [117] between -78° and 16°. Reaction started immediately and vigorously, yielding viscous products of varying molecular weight. The product of reaction at -35° to -40° was ~30% polymers, of molecular weight 280–616 and 50% polymers with molecular weights 3100–4800, and in the product obtained at 7°–16° ~60% had molecular weight 132–270, and 40% had molecular weight 358–686.

Vainshtein and Dintses[118] investigated the action of $AlCl_3$ between -70° and -10° on a cracking gas butane-butene fraction containing 15–30% of isobutene. To prevent the reaction from proceeding violently at the start, the catalyst was deactivated with dichloroethylene, carbon tetrachloride, heptene, or a solution of the butane-butene fraction polymers. The aluminium chloride complex was decomposed by treatment of the reaction products with alcohol at -30°. Reaction at -20° to -30° gave polymers suitable for addition to lubricating oils. The reaction rate increased with increasing $AlCl_3$ concentration over the range 0.15–1%, and thereafter remained constant. At -30° 90% of the isobutene was polymerised in an hour. When reaction temperature was increased from -70° to -10°, the molecular weight of the polymers fell correspondingly from 12 000 to 6000.

Titanium tetrachloride. Isobutene in n-hexane solution[98,115,119] is slowly polymerised by $TiCl_4$ at -90°. The rate of reaction is markedly increased by introduction of moist air (atmospheric air) or moist nitrogen. Addition of small amounts of snow or ice did not initiate reaction. Thus, with $TiCl_4$ an activator, probably water, is essential, but it can only be in the form of water vapour. Evidently this gives highly dispersed crystals which react with $TiCl_4$. Apart from water, small quantities of concentrated H_2SO_4 or 20% oleum can be used as activators for the low-temperature polymerisation of isobutene[119]. However, they cannot be used to study the reaction kinetics, because they form complexes with $TiCl_4$ which are insoluble in hexane. Substances which initiate liquid-phase polymerisation of isobutene by BF_3 at room temperature (acetic acid, diethyl ether), act as inhibitors in the case of $TiCl_4$. But dry trichloroacetic acid[119,120] is an effective activator; it forms the complex $TiCl_4 \cdot CCl_3COOH$ in hexane. In that case the polymerisation is a first order reaction with respect to CCl_3COOH. As the temperature is raised the reaction rate rises linearly, and the molecular weight of the polymers increases with increase of isobutene concentration and catalyst concentration. Picric acid, with a dissociation constant of the same order, did not act as an activator, but it did not retard polymerisation when trichloroacetic acid was added. The scheme given below represents the polymerisation of isobutene in the presence of $TiCl_4$:

(29.1) (29.1a) (29.2) chain initiation

$$MH^+ + M \rightarrow M_2H^+;\ M_2H^+ + (n-2)M \rightarrow M_nH^+,\ \text{chain growth} \quad (29.3)$$

$$\left.\begin{array}{l} M_nH^+ + TiCl_4OH^- \rightarrow M_n^- + TiCl_4 \cdot OH_2, \\ M_nH^+ + TiCl_4OH^- \rightarrow M_nHOH + TiCl_4, \end{array}\right\} \text{chain breaking} \quad (29.4),\ (29.4a)$$

$$M_nH^+ + M \rightarrow M_n + MH^+,\ \text{(reactive centre transfer)}, \quad (29.5)$$

where M is a monomer molecule.

This scheme is also typical of other metal halides. The most probable reaction for chain breaking is (29.4) and not (29.4a), because up to 2000 molecules of isobutene (in the case of BF_3 [121]) can polymerise for each molecule of water present.

Zirconium tetrachloride. Isagulyants and Bonkoi[122] investigated the polymerisation of isobutene by zirconium tetrachloride. At room temperature in the liquid phase (sealed tubes) reaction took place very readily, and oily polymers were formed regardless of the quantity of catalyst present. Increasing the amount of catalyst from 0.2% to 2% raised the polymer molecular weight from 638 to 1336. Isobutene conversion was a maximum with 1% of catalyst, when the polymer molecular weight was 900 and it contained 76–90% of unsaturated material. But when the catalyst concentration was raised to 27%, the quantity of unsaturated material dropped to 33%; this was ascribed to hydropolymerisation.

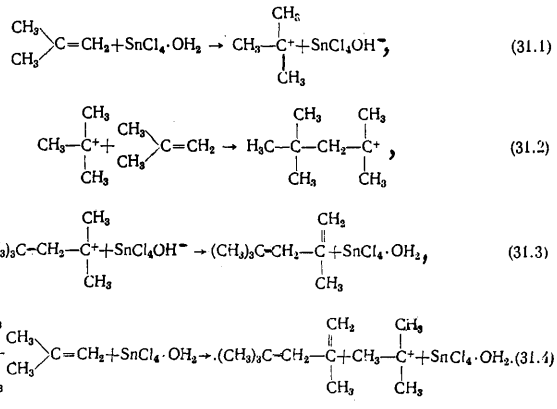
At 100°–200° and 10–70 atm reaction took place very readily with much evolution of heat. Complete conversion of isobutene with minimum catalyst consumption was obtained at 180°, when the resultant polymerisate, comprising almost wholly unsaturated hydrocarbons, boiled at 40°–340°. Diisobutene was the main product. Increasing the proportion of catalyst increased the yield of isomeric hydrocarbons. The dimeric material consisted mainly of 2,4,4-trimethylpent-1-ene (plus a small amount of the -2-ene), 2,3,4-trimethylpent-1-ene, 2,5-dimethylhex-2-ene, and 2,5-dimethylhex-3-ene. Wholly absent were 2,4,4-trimethylpentane, 2,5-dimethylhexane, and 2,3,4-trimethylpentane. A small amount of heavy hydrocarbons was found along with the diisobutenes.

Copolymerisation of isobutene with other alkenes using $ZrCl_4$ + HCl has been described[123].

Stannic chloride. Investigation of the low-temperature polymerisation of isobutene by $SnCl_4$ [124] showed that at -78.5°, with C_2H_5Cl as a diluent, it is impossible to free the system from traces of water even with very careful purification. Polymerisation was very slow; the rate of polymerisation increased as the amount of water added was increased, up to a concentration of 0.5%, but the molecular weight of the polymer fell (from 57 200 at 0.056% H_2O to 51 000 at 0.688% H_2O). But $SnCl_4$ concentration and temperature also had major effects on polymerisation rate. With $SnCl_4$ concentration 1–2% the polymerisation rate was constant and independent of the catalyst concentration. Raising the temperature from -96.5° to -63.5° led to a 25-fold increase in reaction rate; the mean activation energy was 7 kcal/mole. Ethyl alcohol, t-butanol, diethyl ether, and acetone inhibited the reaction. The authors[124] considered that catalytic polymerisation at -78.5° could not occur in the absence of an activator for $SnCl_4$. Initiation of reaction does not consist simply of formation of a complex between stannic chloride and alkene. Apparently an equilibrium is established:

$$SnCl_4 + SnCl_4 \cdot 2H_2O \rightleftarrows 2SnCl_4 \cdot H_2O, \quad (30)$$

a hydrate able to initiate the process being formed. The low temperature polymerisation of isobutene in a solvent (ethyl chloride) can be represented as:



$$(CH_3)_3C{-}CH_2{-}C^+ + SnCl_4OH^- \rightarrow (CH_3)_3C{-}CH_2{-}C(=CH_2) + SnCl_4 \cdot OH_2, \quad (31.3)$$

Hence the initial stage (31.1) of the reaction involves transfer of a proton from a molecule of hydrate to monomer. This can be thought of as involving, at the beginning, a complex with loosened bonds between the hydrate and the monomer. In solvents of low dielectric constant this complex can also exist as an ion pair. Chain growth can be stopped by reaction with a negative ion formed in the initial step [reaction (31.3)], or by proton transfer to monomer, giving rise to a new active centre.

Ferric chloride and bromide. Isobutene polymerisation and copolymerisation with alkenes and alkadienes have been effected in the presence of $FeCl_3$ plus accelerators (H_2SO_4, HNO_3, hexanoic and trichloroacetic acids)[125,126] and also in the presence of $FeBr_3$.[125]

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From the data given in the present section, it is evident that low-molecular-weight polymerisation, taking place above 0°, gives products similar to those obtained when mineral acids are used. Low-molecular-weight polymers are obtained — isobutene dimers, trimers, and tetramers. The reaction is complicated by the side reactions of isomerisation, cyclisation, and hydropolymerisation. Evidently polymerisation of isobutene by acids and metal halides at 0°–400° proceeds by one mechanism. The low-temperature polymerisation of isobutene to polyisobutene by metal halides, occurring below 0°, particularly at -70° to -120°, is very violent and takes place by a chain reaction. Reaction rate depends on catalyst activity. A comparative study of the activity of the catalysts was carried out in 1941–1942 by Fairbrother and Seymour; their results, given in a paper by Polanyi and coworkers[115], are set out in Tables 1 and 2. From these data it is evident that the

TABLE 1. Catalytic activity of metal halides. Initial temperature -78°.

Halide	Amount of catalyst, %	Amount of isobutene, %	Reaction time	Yield of polymer, %	Molecular weight $\times 10^{-3}$
BF_3	0.05	10	seconds	100	120—150
$AlBr_3$	0.05	20	1—5 min	70—90	120—150
$TiCl_4$	0.12—0.25	30	20—70 min	35—50	100—130
$TiBr_4$	1.0—1.5	30—50	12—18 h	30—50	70—90
BCl_3	0.9—1.5	40—50	12—18 h	0.5—1.5	30—50
BBr_3	0.6—1.0	50	12—18 h	0.5—1.5	20—30
$SnCl_4$	1.5—2.5	50	17—50 h	10—18	12—25

TABLE 2. Lower limit of concentration for polymerisation.

Catalyst		$AlBr_3$	$TiCl_4$	$TiBr_4$	BCl_3	$SnCl_4$
Composition of reaction mixture, %	isobutene	1.0	7.0	20	20	10
	catalyst	0.01	0.12	0.50	0.8	1.0

molecular weights of the polymers drop with decreasing activity of the metal halides, the degree of activity changing parallel to the acidity of the halide. In the presence of BF_3 polymerisation is completed in seconds with 100% conversion, with $AlBr_3$ it takes minutes and the conversion is 70–90%, while with $TiCl_4$ many hours are required and the yield is 35–50%. Finally, with $SnCl_4$ days are required, and the yield is 10–20%. Almost all the halides are activated by substances which as a rule have mobile H atoms; e.g. water, t-butanol, sulphuric, acetic, and trichloroacetic acid.

3. Polymerisation by Oxide Catalysts

Aluminosilicates. The polymerising action of aluminosilicates on alkenes was first established by Gurvich[127]. He observed that the unsaturated hydrocarbons present in petroleum lubricating oils, as well as pentene and pinene, were polymerised at room temperature, by a mildly calcined aluminosilicate — floridin. The activity of floridin was a maximum when the water loss was 12–13%, which occurs when it is heated to about 300°.

Lebedev and Filonenko[128] studied polymerisation of isobutene at room temperature in the presence of a floridin whose composition was 55.3% SiO_2, 21% Al_2O_3 + Fe_2O_3, 4.3% MgO + CaO, 1.9% K_2O + Na_2O, and 17.9% H_2O. On heating in air at 275°–325°, the floridin lost 12–12.3% of its moisture, and acquired an increased activity. Polymerisation of isobutene over floridin was also observed by van Winkle[129].

Lebedev and Koblyanskii[6] activated floridin at ~300° for 2 h. Isobutene was polymerised more energetically at -80° than at room temperature, and gave products of high molecular weight. At 200° polymerisation took place with difficulty, and at 290° it was not observed at all. Depolymerisation occurred over floridin at temperatures higher than room temperature, and with triisobutene this was already in evidence at 70°. Increase of contact time increased the yield of high polymers. Gaseous isobutene gave a product containing 18% of dimer, 51% of trimer, and 31% of higher polymers — tetramer, pentamer, and higher. The product obtained by polymerising liquid isobutene over floridin in sealed tubes for 3–24 h contained 4% of dimer, 25% of trimer, and 71% of higher polymers. The dimer, which was identical with Butlerov's diisobutene, was completely polymerised by floridin. The trimer did not polymerise under these conditions, and the pentamer was completely decomposed by floridin at 200° into dimer and trimer. The authors suggested that polymerisation proceeds stepwise according to the scheme

$$C_4H_8+C_4H_8 \longrightarrow (C_4H_8)_2 \xrightarrow[(C_4H_8)_2]{C_4H_8} \begin{matrix}\nearrow (C_4H_8)_3 \xrightarrow{(C_4H_8)_3} (C_4H_8)_5 \\ \searrow (C_4H_8)_4\end{matrix} \quad \text{etc.}, \qquad (32)$$

In view of the inertness of triisobutene and higher polymers to floridin, polymerisation involves only monomer and dimer.

Investigation of the depolymerisation of triisobutene[130] and higher polymers[131,132] by floridin showed that polymerisation of isobutene by that catalyst is reversible. According to Dobronravov and Frost[133] the equilibrium constant for

$$2\ \text{iso-}C_4H_8 \rightleftarrows C_8H_{16}\ \text{(diisobutene)}, \qquad (33)$$

over the temperature range 168°–313°, can be represented by the following semiempirical equation:

$$\log K' = \log \frac{p^2_{C_4H_8}}{p_{C_8H_{16}}} = -\frac{2959}{T} + 6.049 \pm 0.067\ . \qquad (34)$$

Polymers of different molecular weight were depolymerised[130–132] with varying ease. Diisobutene was the most stable: as the molecular weight increased, depolymerisation took place with great facility, forming monomer and dimer. Depolymerisation occurred at an appreciable rate even at 50°, and proceeded readily at 50°–250°. At the same time side reactions were observed: polymerisation of the monomer and dimer formed in the reaction, and, to some extent, hydrogen disproportionation leading to hydrocarbons more unsaturated than alkenes, along with saturated hydrocarbons. Triisobutene was 99% depolymerised, giving diisobutene and 0.5–1% of C_8H_{14} hydrocarbons plus isobutene.

When rubber-like polymers of isobutene were thermally degraded, monomer plus polymers ranging from dimer to pentamer were the sole products. At the same time saturated hydrocarbons, and C_n hydrocarbons, where n was not a multiple of 4, were formed.

Lebedev and Borgman[134] investigated in detail the conditions which were particularly favourable for obtaining high-molecular-weight polymers. Suitable conditions were: use of floridin of decreased catalytic activity, low space velocity, and reaction temperature of -75°. The average molecular weight of the products was 8000. Isobutene was also readily polymerised over a synthetic aluminosilicate catalyst at 40°, to give polymers resembling those obtained with floridin[135]; di-, tri-, and tetramers were obtained.

Slobodin[136] observed that isobutene could be polymerised over a series of bleaching earths. The average molecular weight of the polymer depended on catalyst activity and was less with the more active catalysts. Silica gel did not bring about reaction.

A detailed investigation of isobutene polymerisation over Gayer's synthetic aluminosilicate catalyst was carried out by Kazanskii and Rozengart[137–139]. Polymerisation took place over a wide temperature range, from room temperature to 289°. As the temperature was raised the polymer yield fell; the dimer yield passed through a maximum at ~200° and then fell sharply; the yield of trimer and higher fractions fell sharply. The composition of the polymerised products varied markedly with increase of temperature, and the content of cracking and isomerisation products was raised.

Under the same conditions Butlerov's diisobutene gave a mixture of dimers, trimers, and other isobutene polymers resembling the products obtained by polymerising isobutene over the same catalyst. At 210° depolymerisation of diisobutene to isobutene was also observed. A study of the

effect of adding thorium[137,140] and zirconium[140] to aluminosilicate showed that such triple catalysts are highly active. With them polymerisation took place at 165° and 45 atm. All catalysts were readily regenerated by air at 400°–500°, and the activity of the regenerated catalyst was somewhat higher than that of fresh catalyst. Zinc and thallium have also been mentioned as additives to aluminosilicate catalyst[137]; they deactivate it, as do cobalt and nickel[141-143]. Isobutene has been polymerised over $Al_2O_3-SiO_2-Ni$ at 250°–350° and 4–10 atm[141].

Kazanskii and Rozengart[137] found that the compositions of the products of polymerisation by synthetic aluminosilicate catalyst and "solid" phosphoric acid closely resembled one another. For this reason they ascribed the polymerising capacity of aluminosilicates to their acid properties, and assumed an ionic mechanism for polymerisation of alkenes by such catalysts, a view which was later supported by other workers[144]. The activity of these catalysts, being due to the presence of protons, vanished on neutralisation of the surface acids by absorption of basic compounds[145-148]. It is assumed that the active complex is $(HAlSiO_4)_x$.[147]

Other oxide catalysts. Rapoport et al.[149] carried out one-stage isobutene polymerisation with subsequent dehydrocyclisation of the polymerisation products over $MoO_3-Al_2O_3$ at 300°–450° and atmospheric pressure. In the xylene fraction of the product obtained at 400°, there was 60% of *p*- and *m*-xylenes, a yield of 6 g/m³ of feed gas. At 200° isobutene was polymerised to di- and triisobutenes.

With 1–2% BeO [83,84] isobutene was polymerised at 275°, the yield being 25%. The main product was diisobutene, plus small amounts of triisobutene. Polymerisation took place readily over activated bauxite[150-152] at 120°–175°, both at atmospheric and at higher pressures. Isobutene was not polymerised when passed over Al_2O_3 at 600° [89]. In the presence of Al_2O_3 + HCl [153] isobutene dimerised to give 29.6% of dimer when the initial isobutene concentration was 89.8%. Removal of oxygen from the starting isobutene raised the dimer yield to 45%, while increasing the pressure to 2.5 atm had almost no effect on the dimer yield.

The following conclusions can be drawn from the investigation of the polymerisation of isobutene on oxide catalysts: polymerisation over synthetic and natural aluminosilicates takes place over a wide temperature range, -80° to 290°. Silica gel and Al_2O_3 do not bring about polymerisation, but isobutene is polymerised by Al_2O_3 + HCl.

4. Polymerisation by Alkali Metals

Ostromyslenskii[154] investigated the polymerisation of alkadienes mixed with alkenes by metallic sodium (anionic polymerisation). L'vov showed[155] that when a butadiene–isobutene mixture was polymerised with 2% Na metal, at 20°–25° under nitrogen, the isobutene partly reacted. When the isobutene concentration was increased the relative yield of polymers also rose, and was equivalent to 120 vol.% with respect to butadiene taken when the mixture contained 88% of isobutene. But the product also contained more low polymers (30% in the case mentioned). Among them was a product of addition of isobutene to butadiene, namely 2-methylhepta-1,5-diene, and aliphatic hydrocarbons $C_{12}H_{20}$, $C_{16}H_{28}$, $C_{20}H_{32}$, and $C_{24}H_{38}$, all of which had the general formula $(C_4H_6)_{n-1}C_4H_8$, with *n* double bonds per molecule, (*n* - 1) molecules of butadiene and one molecule of isobutene having reacted.

L'vov considered that polymerisation of butadiene–isobutene mixtures can readily be explained by a chain theory[155]; the formation of low polymers is related to chain termination in the butadiene polymerisation by isobutene reacting with active molecules of growing polymer. A suggested chain termination mechanism[156] is based on the assumption that hydrogen atoms in isobutene can be substituted by metallic sodium, through the agency of active sodio-organic compounds which are formed from Na and the alkadiene:

$$Na(C_4H_6)_nNa + 2\,\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C{=}CH_2 \longrightarrow 2CH_2Na{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + H(C_4H_6)_nH \qquad (35)$$

A similar mechanism was observed[157] when isobutene was copolymerised with isoprene under the influence of sodium. With 3% metallic Na, the overall yield of polymer reached 117% with respect to the initial isoprene when the isobutene concentration was raised to 90%, and at the same time the content of low-molecular-weight copolymers increased. Hydrocarbons C_9H_{16} and $C_{14}H_{24}$, products of addition of one molecule of isobutene to one and two molecules of isoprene, were isolated. Copolymerisation of isobutene with ethylene and propene, in the presence of metallic sodium, was observed[158] at 300° and 500–600 atm. A hexene was isolated from the low molecular products derived from isobutene plus ethylene, and a heptene from those derived from isobutene plus propene.

5. Polymerisation by Organometallic Compounds

Ziegler[159] claimed that isobutene was polymerised by $AlCl_2C_2H_5$, though more feebly than by $AlCl_3$, and that it was not polymerised at all (unlike ethylene) by $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$. Topchiev, Krentsel', and coworkers[160] found that polymerisation of isobutene with formation of liquid and rubber-like products took place when $Al(C_2H_5)_3$ + $TiCl_4$ was used. Reaction occurred between -25° and 75° in isooctane, at a molar ratio $AlEt_3 : TiCl_4 = 1 : 2$, the concentration of dissolved $AlEt_3$ being 1 wt.%. The yield of polymers was up to 80% of the initial isobutene and 95% of that reacted. The molecular weight of the polymers increased as the temperature was lowered, from 2000–3000 at +50° to 10 000 at -25°. Reaction time and the $AlEt_3 : TiCl_4$ ratio also affected the molecular weight[161].

6. Hydropolymerisation of Isobutene

Ipat'ev and Komarevsky[162] stated that isobutene and pentene give respectively octane and decane with $Fe-MgCl_2$ catalyst and hydrogen at 250°–300° and 80 atm, and they called the reaction hydropolymerisation. They supposed that the reaction consists of two stages: alkene dimerisation and dimer hydrogenation. NiO can be used instead of Fe, and $ZnCl_2$ or $AlCl_3$ in place of $MgCl_2$. The yield of isobutene polymerisate was 50–90% of the isobutene, depending on the catalyst, and the hydropolymerisate comprised mainly hydrodimer and hydrotrimer.

Eidus and Nefedov[163] found that addition of hydrogen to isobutene substantially affects the course of its polymerisation over a Co-clay catalyst at 190° and atmospheric pressure. Even a small addition of hydrogen, 0.2%, caused considerable increase in polymer yield and in degree of polymerisation. Raising the hydrogen concentration to 50% led to further increase in polymer yield and promotion of the hydrogenation and hydrocracking side reactions. This effect of hydrogen was not observed over a

red clay carrier, though the latter was more active than the Co–clay catalyst, and led to formation of isobutene dimers and trimers. It was shown[164] that the course of hydropolymerisation of isobutene over Co–clay varied with the H_2 content of the feed gas. With no hydrogen, or with a concentration of 0.2–0.3%, the main products were isobutene dimers and trimers, and the reaction mechanism was ionic. At 40–50% hydrogen concentration the main reaction products were 2-methylalkanes and 2-methylalkenes (2-methylbutane, 2-methylpentane, 2-methylhexane, etc., and the corresponding alkenes). In this case reaction evidently involved free radicals formed in the presence of the reduced cobalt.

III. INDUSTRIAL APPLICATION OF PROCESSES FOR POLYMERISING ISOBUTENE

Polymerisation processes involving isobutene are of great practical importance. Thermal polymerisation of alkenes in cracking gases offers a ready method of making liquid motor fuels. The process is operated at 480°–540° and 50 atm, and the resultant gasoline has octane number 75–80.[165]

Sulphuric acid polymerisation of a butene–butane fraction is effected with 60–70% acid either at -20° to +25°, which brings about selective dimerisation of the isobutene, or at 75° to 110°, when the n-butenes also react. The resultant dimer is hydrogenated to isooctane[166–176].

Sulphuric acid is also used to copolymerise isobutene with other alkenes, n-butenes[177], and isopentenes[178,179]. A mixture of octenes and octanes is obtained by polymerising isobutene under the influence of SO_2 at 400° and 182 atm[180]. Anhydrous SO_3 is used as a catalyst for the preparation of low-molecular-weight isobutene polymers[181].

In addition to sulphuric acid, phosphoric acid[182] is used industrially as a catalyst for making high-octane motor fuels and technical isooctane from technical butane–butene mixtures. It is used as the "solid" acid (phosphoric acid on a carrier), in liquid form, or as copper pyrophosphate. Polymerisation of isobutene alone or copolymerisation with other alkenes over a catalyst (e.g. phosphoric acid on a carrier) is usually effected at 50°–200° and 17–63 atm. Carriers for phosphoric acid are: silica gel[183], activated carbon[65], and kieselguhr[184–186]. For example, copolymerisation of isobutene with propene over phosphoric acid[182,187–189] is effected at 135° and 35–42 atm, and copolymerisation with n-butenes at 128°–175°.

Phosphates used as catalysts are[190–194]: phosphates of zinc (solution in H_3PO_4[190,191]), of calcium, copper, cadmium (in H_3PO_4[192]), and cerium[194]. Reaction takes place at 120°–285°, sometimes under pressure (up to 98 atm). For example, with the copper phosphate, selective polymerisation of butene–butane mixtures is carried out at 250° and 60 atm[195,196]. The temperature for non-selective polymerisation is 190°–205°.

It is possible to obtain isomeric octanes by hydropolymerising isobutene at 250°–300° with a hydrogen pressure of 80 atm, using a solid catalyst, phosphoric acid-nickel(II) oxide-iron, when 92–96% of the isobutene reacts, the liquid polymerisate containing 46–56% of octanes, octane number 83–84.[121]

The low-temperature polymerisation of alkenes, and in particular isobutene, in the presence of metal halides, is of great practical importance, because it allows the production of high polymers, which are lubricating oils, lubricating-oil additives, and synthetic rubbers and plastics[79].

Low-temperature polymerisation is usually effected in the liquid phase with a diluent and 0.1% (with respect to the isobutene starting material) of catalyst. Isobutene is polymerised alone or copolymerised with alkenes[123,125,197–202], conjugated alkadienes[126,200,203–222], cycloalkenes[223–227], and alkyl acetylenes[209]. Suitable diluents are: alkyl halides[125,226–231], carbon tetrachloride[199,232], aliphatic esters[233,234], ketones[123,235,236], ethers[226*], nitrous esters[236,237,238], hydrocarbons[123,125,198,199,236–241], alcohols[213,242,243], carbon disulphide[231,244], and carbon dioxide[209]. The following can be used to accelerate reaction: sulphuric acid, nitric and trichloroacetic acids, formaldehyde, phenol, cresol, aliphatic, cycloalkyl, and aromatic alcohols[126], carbon dioxide, ethers[234], and hydrogen halides[245]. Sometimes up to 1% of a catalyst poison (S, H_2S, or organic sulphur compounds) is added[241,246]. Addition of hydrogen halides, anhydrous HF or HCl can lower the molecular weight of the polymer, although at room temperature such compounds facilitate polymerisation of alkenes by metal halides, which is often carried out in emulsions.

Emulsion polymerisation has a number of advantages: possibility of better control of the process, prevention of overheating, preparation of homogeneous hydrocarbons, etc. It can be applied only in a limited temperature range, which can, however, be extended by employing media of fluorohydrocarbons, e.g. perfluoro-*m*-xylene, and a mixture (1:3) of perfluoromethylnaphthalene and perfluoromethylcyclohexane[247]. Both of these solvents remain liquid between -95° and 80° and do not mix with the isobutene or butadiene at temperatures below the boiling points of these hydrocarbons; in addition, polymerisation catalysts ($AlCl_3$, BF_3) have practically no action on them at room temperature or below. Polymerisation takes place readily at -70° in a well-mixed emulsion system when the catalyst is introduced in a finely-divided state or dissolved in the perfluorohydrocarbon or in ethyl chloride. Isobutene is usually copolymerised with butadiene. The molecular weight of the polymerisation products falls considerably as the butadiene content of the starting mixture is increased. Low-molecular-weight copolymers are obtained when isobutene is copolymerised with isoprene or 2,3-dimethylbuta-1,3-diene.

An example of the industrial use of low-temperature polymerisation is the process for making Oppanol. This is carried out with BF_3 at -80° to -90° using a diluent (usually isobutane). Depending on the solvent : isobutene ratio, either a lubricating oil or a solid plastic material (Oppanol, Vistanex) is obtained. Various aspects of the process are discussed in the patent literature[106–109,197,198,232–234,248–268]. There is also an industrial process for polymerising isobutene plus 2% alkadiene, using $AlCl_3$ as a catalyst, to give a synthetic rubber (butyl rubber)[269–273]. The process is carried out at -90° to -100° using a diluent (methyl chloride). The catalyst for polymerisation and copolymerisation with other unsaturated compounds may be $AlCl_3$[90,123,125,126,197–208,221–230,235,242,261–263,274–285] as well as $AlBr_3$[125,126,209,229,281], $AlBrCl_2$, $AlBr_2Cl$, and the complexes $Al(OC_2H_5)_3 \cdot 3AlCl_3$[215]; $AlOBr \cdot 4AlBr_3$[200,209,229,276]; $AlBr_2I \cdot AlOI$, $AlBr_3 \cdot AlOBr$, $4AlBr_3 \cdot AlOBr$, $6AlBr_3 \cdot AlOBr$, $4AlBr_3 \cdot TiOCl_2$[200,286]; $AlCl_2OH$[229,230], $AlBr_2OH$, $AlBr_2Cl \cdot AlOCl$[229], $AlBrCl_2 \cdot AlOBr$, $AlBr_3 \cdot Br_2CS_2$[278], Al_2ClBr_5[240], $AlCl_3 \cdot CH_3OCH_3$[235,236], $AlCl_3 \cdot C_2H_5COCH_3$[235], $AlBrCl_2 \cdot AlOBr$, $AlCl_3 \cdot Al(OC_2H_5)_3$, $AlBr_3 \cdot AlBr_2OH$[229], and $TiCl_4$[98,125,126,197,229,237,254,276] and its complexes:

* Ethers are not mentioned in ref. 226 (Ed. of Translation).

$TiCl_2(COCH_3)_2$, $TiCl_3(COCH_3)$ [287], $TiCl_4 . AlCl_2OH$, $TiOCl_2 . TiCl_4$ [229], and $SnCl_4$ [123,126].

The information given above shows that polymerisation and copolymerisation of isobutene are widely used industrially. Of special importance are processes for polymerising isobutene and butane–butene mixtures to yield technical isooctene (subsequently hydrogenated to isooctane), using sulphuric and phosphoric acids, and low-temperature polymerisation processes involving isobutene with a Gustavson–Friedel–Crafts type of catalyst (BF_3, $AlCl_3$) for making high quality lubricating oils, synthetic rubbers, and plastics.

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MACROMOLECULAR DIELECTRICS

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INTRODUCTION

If a polymer is to be used as an electrical insulator or a dielectric, not only its electrical properties but also a number of other physicochemical properties must fulfil certain conditions. The fact that a given polymer has certain electrical properties is no guarantee that it will be of any practical use. For example, some polymers are ruled out because their thermal stability is poor, because they are difficult to work, or because their mechanical strength is low.

Our aim in this paper is to demonstrate certain regularities in the electrical properties of polymers, using data from our own publications and from those of other investigators. Attention will mainly be directed to dielectric loss and polarisation, and their relation to the structure of the polymers. In this connection we shall not only consider the chemical composition, stereochemical structure, and crystalline or amorphous state, but also the nature of the thermal motion, since the latter has a marked effect on the electrical properties. The main peculiarity of the thermal motion of a polymer macromolecule is that, because of its chain-like structure and relatively enormous dimensions, intramolecular thermal motions play an important part.

Polymers may be divided into polar and non-polar, according to the stereochemical structure of the monomers; the overwhelming majority are polar. The variation of the electrical properties of polar polymers may be explained in terms of the nature and strength of the molecular forces. Study of the effective dipole moment of these polymers has shown that intramolecular forces are predominant[1], while in substances of lower molecular weight the intermolecular forces are most important.

A number of the electrical properties of polymers are kinetic in nature, so the study of these substances in changing electrical fields is of great interest. This is also worth while from the practical point of view, because dielectrics are used more often in alternating than in constant electric fields.

1. DIELECTRIC LOSSES AND POLARISATION OF NON-POLAR POLYMERS

Non-polar polymers are extensively used as high-frequency dielectrics. The most important electrical properties of such substances are the tangent of the dielectric loss angle, $\tan\delta$, and the dielectric constant ϵ'.

We shall first consider the dependence of these quantities on frequency and temperature for the most widely investigated polymer, amorphous polystyrene (PS).

Fig. 1 shows $\tan\delta$, ϵ', and n_D^2 (the square of the refractive index) for PS as functions of temperature at a frequency of 10 kc/s,[2] and $\tan\delta$ and ϵ' as functions of frequency at two temperatures, one below and one above the vitrification temperature, $T_{vit} = 80°$. It may be seen from Fig. 1*b* that $\tan\delta$ and ϵ' are practically independent of the frequency for vitreous PS (i.e. for $T < T_{vit}$). The value of $\tan\delta$ is $(0.5-1) \times 10^{-4}$, and this does not vary much with the temperature for $T < T_{vit}$. The decrease of ϵ' on heating in this temperature range is connected with the thermal expansion of the sample. Thus, it may be seen from Fig. 1 that there is a break in the ϵ' vs. T curve at about the vitrification temperature, which is also found in the density vs. temperature curve. The values of ϵ' and n_D^2 for PS coincide within 1% over a wide range of temperatures.

All this shows that relaxation-dependent dipolar dielectric losses do not occur in vitreous PS. It may also be seen from Fig. 1 that at temperatures above T_{vit}, the $\tan\delta$ vs. T and $\tan\delta$ vs. $\log f$ curves both show maxima. Near these maxima the value of ϵ' begins to decrease with the frequency and increase with the temperature. These are signs of dipolar polarisation. The presence of dipoles in PS may be due either to impurities chemically bound to the chain or to the slight polarity of the monomer ($\mu \sim 0.1-0.3$ c.g.s. units).

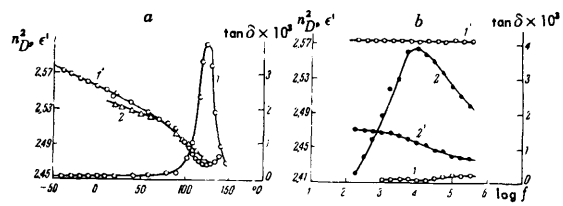


Fig. 1. The dielectric constant, square of the refractive index, and tangent of the dielectric loss angle of polystyrene as functions of temperature (*a*) and frequency (*b*)[2]. *a*: 1), 1') $\tan\delta$ and ϵ' at 10^3 c/s; 2) n_D^2. *b*: 1), 1') $\tan\delta$ and ϵ' at 39°; 2), 2') $\tan\delta$ and ϵ' at 134.5°.