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Institute of Chemical Physics,
Academy of Sciences of the
USSR, Moscow

U.D.C. 547.313.6

# CHEMICAL REACTIONS OF DIENE POLYMERS

I.A.Tutorskii, S.V.Novikov,
and B.A.Dogadkin

CONTENTS

I. Introduction 881

II. Addition to a double bond 881

1. Reactions with compounds containing a mercapto-group 881
2. Reaction with hydrogen halides 883
3. Hydrogenation 884
4. Reaction with perbenzoic acid 885

III. Reactions involving the participation of double and allyl bonds 886

1. Reaction with ethylenic monomers 886
2. Reaction with aldehydes 887
3. Reaction with molecular chlorine 888
4. Reaction with bromine and other halogenating agents 890

## I. INTRODUCTION

Diene polymers are now the most widely used of all known polymeric materials. The polymerisation of dienes leads to the production of elastomers which acquire all the necessary properties during further treatment (plasticising, vulcanising). In addition to the problem of the processing and modification there is the problem of stabilising the polymer material. The effective solution of these problems is impossible without a knowledge of the chemical nature of the polymers used.

It is necessary to point out that there has not yet been any detailed investigation of the reactivity of diene polymers as a class of organic compounds. Most of the studies in the field of the chemistry of diene polymers are of an applied nature and are connected with the study of the vulcanisation and stabilisation of polymers or are directed to the study of individual reactions of diene polymers, such as chlorination, hydrochlorination, etc. At the same time, without knowing the general features of the chemistry of diene polymers it is impossible to carry out effectively work of an applied character, directed to the solution of particular practical problems.

The present review aims to be a critical consideration and systematisation of the published information on the chemistry of diene polymers up to the end of 1965. An attempt has been made to find the characteristics of the double bonds in polymers having a regular 1,5-polyene structure. The review does not attempt a detailed examination of the information on vulcanisation and oxidation that has appeared in monographs.

## II. ADDITION TO A DOUBLE BOND

### 1. Reaction with Compounds Containing a Mercapto-Group

The reactions of hydrogen sulphide and thiols with alkenes have been studied in detail by Naylor [1]. Under the catalytic action of sulphur, hydrogen sulphide is readily added at the double bond of polyisoprene in accordance with the Markovnikov rule. The thiol formed can react with another double bond to give a sulphide. The oxidation of two thiols leads to the formation of a disulphide. As a result of the last two reactions, cross-linking of the macromolecules of the rubber takes place. In the presence of a peroxide or on ultraviolet irradiation, hydrogen sulphide adds at the double bond of polyisoprene contrary to the Markovnikov rule.

The addition of alkyl and aryl thiols to a double bond also proceeds in accordance with the Markovnikov rule in the presence of sulphur and contrary to the rule when the reaction is carried out in the presence of peroxide [2]. The easier it is for homolytic rupture of the S–H bond, the greater the acidity of the thiol, and the more active the thiol relative to the double bond. Prilezhaeva and Shostakovskii [3] give the following series for the activity of thiols in relation to alkenes:

$$C_6H_5SH > HOOC.CH_2SH > RCH_2SH > R_2CHSH > R_3C.SH.$$

Electron-donating groups in the thiyl [mercapto-] radical reduce its reactivity towards double bonds; electron-withdrawing groups, on the other hand, increase its activity. A drop in the electron density of the double bond leads to a decrease in its reactivity towards thiols.

Conjugated, vinyl, terminal double bonds, and also double bonds in rings react readily with thiols, but inner non-conjugated double bonds are less reactive towards thiols[4].

Natural rubber exhibits a low reactivity towards thiols. It does not react with ethyl thiol, isopentyl thiol, thiophenol[5], or tri- and hexa-methylenedithiols[6] when the reaction is performed in an inert medium in the presence of peroxide or under ultraviolet irradiation. At the same time the addition of thiols to low-molecular-weight alkenes, which model the structure of polyisoprene, does take place under analogous conditions. Cunneen found the following series for the activity of alkenes in relation to thiols: cyclohexene > dihydromyrcene > squalene > natural *cis*-polyisoprene.

The addition of thiols to the double bonds of diene polymers takes place when atmospheric oxygen participates in the reaction as a third component or when the reaction is carried out in latex. Hull and coworkers[7] vulcanised natural rubber on rollers in air with the aid of aliphatic and aromatic dithiols, inert relative to polyisoprene when the reaction is carried out in a solvent in the absence of atmospheric oxygen. Foxly[8] notes the reactivity of dodecanethiol towards polyisoprene when the reaction is performed in solution in the presence of oxygen, whereas in an inert medium these substances do not react. Dogadkin and coworkers[9] observed the reaction of thiols with polyisoprene in the presence of oxygen and the absence of reaction between them in an inert medium, even at elevated temperatures. Pierson and coworkers[10] achieved a high saturation of polybutadiene with methanethiol by carrying out the reaction in latex with an excess of the thiol at 30–60°C in the presence of azoisobutyronitrile. Serniuk and coworkers[4] described the reaction of ethanethiol with diene polymers in latex.

The reaction of thioglycollic acid and its derivatives with diene polymers has received considerable attention. It was found that when the reaction of natural polyisoprene with thioglycollic acid[5] and its esters[11,12] was carried out in an inert medium, over a wide range of temperatures, in the presence of initiators (azoisobutyronitrile, cumene hydroperoxide), and with ultraviolet irradiation, addition of the above thiols at the double bond did not occur. Nevertheless thioglycollic acid adds readily to cyclohexene, 1-methylcyclohexene, and dihydromyrcene in the presence of peroxides at room temperature, and to squalene under ultraviolet irradiation[5]. Ethyl thioglycollate adds to isopentene to 67% extent and to dihydromyrcene to 30%, but does not react with natural *cis*- and *trans*-polyisoprenes under the same conditions[11,12].

Such difference in the reactivity of the polyisoprenes and model low-molecular-weight compounds to relatively weak electrophilic agents is explained by the mutual influence of the double bonds in the 1,5-polyene systems, leading to a decrease in their electron density[13].

From the standpoint of classical chemistry, the possibility of the mutual influence of double bonds through two C–C bonds, and especially through three, is inadmissable. However, the experimental results show that a methylene bridge is not a serious impediment or high barrier for the conjugation of a chain[14]. As Voevodskii and coworkers found by the EPR method[15,16], this interaction of double bonds is also possible where there is an ethylene bridge. The establishment of the mutual interaction of double bonds through one C–C bond is accompanied by considerable drop in the energy of the molecule (5–50 kcal mole$^{-1}$). For the 1,5-diene this interaction energy is appreciably less, but nevertheless sufficient to show the significant influence of the double bonds on reactivity[15]. On going from a 1,5-diene to a 1,5-polyene system the energy of the mutual influence of double bonds increases, which appears as the observable drop in reactivity.

The inertness of the polyisoprenes to thioglycollic acid and its esters does not appear when atmospheric oxygen[17,18] participates in the reaction as a third component or when the reaction is effected in latex[4,19]. In the latter instance the reaction is apparently catalysed by the substances of the non-rubber part of the latex globules. The mechanism of this catalysis has not been discussed in the literature.

Cunneen[20] studied the reaction of thioacetic acid and its chloro-derivatives with natural *cis*-polyisoprene and with model compounds. Thioacetic acid adds quantitatively to polyisoprene in benzene on ultraviolet irradiation for several hours. In the absence of radiation the reaction does not occur even at 100–130°C. Monochlorothioacetic acid adds quantitatively to polyisoprene in the dark in the presence of ascaridole. Ultraviolet radiation accelerates the reaction. The reaction of polyisoprene with di- and trichlorothioacetic acids takes place similarly.

A comparison of the reactivity of double bonds in polyisoprene, cyclohexene, dihydromyrcene, and squalene towards thioacetic acids showed that the order of activity of these alkenes is as found for reaction with thiols.

Ritter[21,22] gives the following series for the activity of thio-acids towards natural *cis*-polyisoprene: thiocaprylic > > thiobenzoic > thio-2-naphthoic > thioacetic > thiostearic > trichlorothioacetic acid. The reaction was effected in xylene (6% solution of the polymer) in two stages. In the first stage a slight excess of the thio-acid was introduced, and the reaction was carried out at room temperature in carbon dioxide atmosphere, in the light for a week. In the second stage the product reacted with a 25% excess of the thio-acid for 8 days at room temperature in the light, in carbon dioxide atmosphere. The finding that thioacetic acid is more reactive than trichlorothioacetic contradicts Cunneen's results[20] and seems doubtful to us.

Dithioadipic and dithiosebacic acids[6] add to natural *cis*-polyisoprene on rolling, leading to cross linking of the macromolecules. Peroxides and ultraviolet irradiation accelerate the reaction. The reaction of dithioadipic acid with polyisoprene in benzene (10% solution of the polymer) reaches 45% at 100°C.

The dithio-acids obtained as a result of the replacement of both oxygen atoms of the carboxyl group by sulphur do not add to natural *cis*-polyisoprene[21].

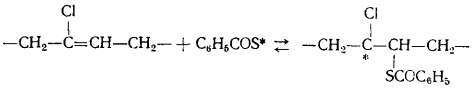
The reaction of thiobenzoic acid with natural *cis*- and *trans*-polyisoprenes has been investigated in detail[11,12,23]. The reaction was effected in an inert medium (argon), in xylene and chlorobenzene, over a wide range of temperatures (20–125°C) and concentration range 0.05–1.0%. The polymer and thio-acid were taken in an equimolecular ratio with cumene hydroperoxide as initiator of the reaction. The reaction proceeds by a radical mechanism, and the extent of the reaction is proportional to the amount of initiator; the temperature dependence has a maximum at about 60–80°C. There is an anomalous dependence of the extent of reaction on the concentrations of the reactants, with a maximum at 0.1–0.3%, this being connected with the

association of macromolecules of polyisoprene in this concentration region. A significant difference in reactivity between *cis*- and *trans*-polyisoprenes to thiobenzoic acid was not observed.

The amount of thiobenzoic acid in the high-molecular-weight fraction of the reaction products greatly exceeds the mean consumption of the thio-acid in the reaction, which is possible only under the non-statistical occurrence of the reaction of polyisoprenes with thiobenzoic acid. The non-statistical nature of the addition of thiobenzoic acid to polyisoprenes is the result of the development of a reaction by an intramolecular chain mechanism. As noted above, in 1,5-polyene systems there is interaction of the double bonds, leading to a drop in their reactivity. The addition of molecules of the thio-acid at one double bond in such a system leads to an increase in the electron density at two neighbouring double bonds owing to the breakdown of the conditions for their interaction. Hence a single act of addition leads to the activation of two double bonds. The probability of addition of subsequent molecules of thio-acid at such double bonds increases, and subsequently the addition of thiobenzoic acid takes place selectively, that is, it is not a random double bond that reacts, but a double bond in the vicinity of the one that has already reacted. The disappearance of an activated double bond during the reaction in turn leads to the activation of a new double bond. Conditions are created for the development of a chain intramolecular mechanism of reactions of 1,5-polyene systems.

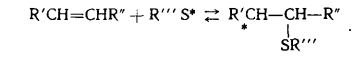
An investigation of the reaction of polychloroprene with thiobenzoic acid[24] showed the influence of the strongly electronegative atom of chlorine located at the double bond, on the reactivity of double bonds regularly alternating in the 1,5 positions. Whereas the addition of thiobenzoic acid to polyisoprenes takes place by a radical mechanism, with polychloroprene this mechanism is not realised. The introduction of up to 12 mole % cumene hydroperoxide into the reaction mixture has no effect on the rate or extent of reaction.

Evidently the macroradical which is formed as a result of the addition of a thioyl radical at a double bond:



is considerably stabilised by the action of the electronegative chlorine atom and is incapable of continuing the reaction chain. An ionic mechanism for the reaction is also excluded, since the dielectric constant of the solvent, when varied within wide limits, has no influence on the rate or extent of the reaction. It was suggested that the addition of thiobenzoic acid at the double bond of polychloroprene takes place with the formation of an intermediate molecular complex.

Sivertz and coworkers' kinetic studies[25-28] showed the addition of a thiyl radical at a double bond to be highly reversible when the reaction took place in the gas or liquid phase:



As a result of the decomposition of the intermediate complex the double bond is regenerated in either the *cis*- or the *trans*-configuration. In the reaction of methanethiol with but-2-ene the rate of decomposition of the intermediate complex to form *trans*-butene is four times that to form the *cis*-butene and 80 times the rate of formation of the addition product. The high reversibility of the addition of thio-compounds at double bonds is responsible for the isomerisation of the double bonds in such reactions.

Cunneen and Shipley[29] observed the isomerisation of natural *cis*-polyisoprene during its reaction with thio-acids. Small quantities (0.1–1.0%) of chlorothioacetic, trichlorothioacetic, and thionaphthoic acids were used. The reaction was carried out in solution and in latex, under vacuum, without a catalyst, for 6 h at 100°C. Thionaphthoic acid was the most effective.

The isomerisation of the natural *cis*- and *trans*-polyisoprenes in their reaction with thiobenzoic acid was studied on rollers, in solution, and in latex[30,31]. The equilibrium ratio of *cis*- and *trans*-structures in the isomerised products was found to be 43 : 57. The high efficiency of the isomerising agent is noted—a considerable degree of isomerisation is obtained when the system has one molecule of thiobenzoic acid per 1270 isoprene links. Monochlorothioacetic, trichlorothioacetic, thionaphthoic, thiosalicylic, and thiostearic acids had similar effectiveness as isomerisation agents[32].

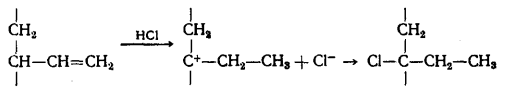
Results on the isomerisation of *cis*-polybutadiene in the presence of thio-compounds are somewhat contradictory. Golub[33] and Seely[34] consider that in equilibrium isomerisation the *cis*- and *trans*-isomers reach a ratio of 5 : 95. Berger and Buckley[35], on carrying out the isomerisation of *cis*- and *trans*-polybutadiene after Golub, found the equilibrium ratio of the *cis*- and *trans*-structures to be 25 : 75. The isomerisation was performed in solution at 25°C, with benzene and toluene as solvents. The isomerisation agents were thionaphthoic acid and diphenyl sulphide, the reaction was carried out under ultraviolet irradiation. The rate of isomerisation increased with the polymer concentration and with the intensity of the radiation; it was independent of concentration of the isomerising agent in the range 1–10 g litre$^{-1}$.

## 2. Reactions with Hydrogen Halides

The reaction of natural *cis*-polyisoprene with hydrogen fluoride was described by Tom[36]. The reaction was carried out in solution at temperatures between −26° and +40°C. In the addition of hydrogen fluoride to the double bonds considerable cyclisation is observed, brought about by the back reaction which eliminates HF, and with rise in temperature the rate of cyclisation increases. At 40°C, there is no addition, only cyclisation. The final product always contains some unreacted double bonds. The best solvent for the addition is xylene; there is considerable cyclisation in benzene and toluene; addition does not take place in carbon tetrachloride and chloroform. In xylene at −26°C the hydrogen fluoride added is 70% of that theoretically possible, and 25% of the double bonds participate in the cyclisation. The temperature and time dependences of the extent of the addition reaction are curves with a maximum.

The reaction of diene polymers with hydrogen chloride has received considerable attention. Hydrogen chloride adds readily to natural *cis*-polyisoprene at moderate temperatures in the bulk, in solution, and in latex[37]. In the presence of peroxide the addition proceeds by a radical mechanism contrary to the Markovnikov rule[38,39]. Synthetic polyisoprene[37] gives a product with incomplete addition. The methylated double bonds in polyisoprene are more reactive than the double bonds of polybutadiene.

As a result of the addition of hydrogen chloride to polyisoprene a tertiary chloride is formed. The vinyl bonds in polybutadiene can also form a tertiary chloride thanks to the Whitmore rearrangement:



Staudinger[40] found a considerable decrease in the viscosity of solutions of natural *cis*- and *trans*-polyisoprenes during hydrochlorination and showed that this is the result of cyclisation taking place simultaneously with addition.

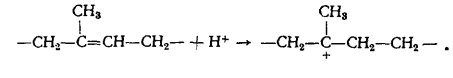
The formation of intramolecular rings during hydrochlorination of natural rubber was also observed by Gehman[41]. Later investigations were quite contradictory and indicated that either there is complete cyclisation during hydrochlorination with subsequent ring opening under the action of HCl[42] or the reaction is restricted to addition and *cis*–*trans*-isomerisation, and cyclisation does not take place at all[43,44]. This conclusion was reached by the authors from calculations of the balance of the double bonds in the reaction products. The sum of the remaining double bonds and the bonds which had disappeared as a result of the addition of chlorine is equal to the degree of unsaturation of the original polymer. Golub and Heller[45] showed, with the aid of high-resolution NMR, that hydrochlorination of natural rubber and balata is accompanied by cyclisation, whereas *cis*–*trans*-isomerisation takes place to a negligible extent or does not occur at all.

In the reaction of 3,4-polyisoprene with hydrogen chloride[46] a predominantly monocyclic structure is formed, with the addition of one molecule of HCl to two double bonds. The cyclohydrochlorination of 3,4-polyisoprene proceeds by an ionic mechanism. Support for the formation of a monocyclic structure is provided by the proportion of chlorine in the reaction products and also by the results of NMR and infrared spectroscopy.

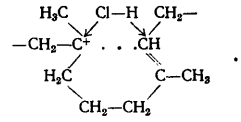
Whereas the cyclohydrochlorination of 3,4-polyisoprene takes place at 10–80°C, the analogous reaction for 1,2-polybutadiene requires much more severe conditions. The product of the cyclohydrochlorination of 1,2-polybutadiene also has a monocyclic structure.

van Veersen[47] investigated the influence of solvents on the hydrochlorination of natural *cis*-polyisoprene. When the reaction takes place in toluene the kinetic curves are smooth. In a mixture of toluene with ethyl acetate or dioxan, the reaction shows a definite induction period. The appearance of an induction period was associated by van Veersen with the reaction proceeding through the intermediate stage of the formation of a $\pi$-complex. Competition by oxygen-containing solvents, which can also form $\pi$-complexes with hydrogen chloride, also leads to the appearance of the observed induction period for the reaction. The negative temperature coefficient of the reaction is also considered as proof that the reaction proceeds through the formation of a $\pi$-complex[47,48].

Gordon and Taylor[49] assume that the addition of hydrogen chloride to *cis*-polyisoprene proceeds via the formation of an intermediate carbonium ion, as occurs in the cyclisation. In accordance with the suggested scheme of reaction a proton is added at the double bond to form a carbonium ion:



The latter forms a pseudocyclocarbonium ion:



Next a neutral molecule of hydrogen chloride is added at the pseudobond. The latter act leads to the regeneration of the carbonium ion. In accordance with this scheme the addition of neutral molecules of hydrogen chloride at the double bonds of polyisoprene, which alternate regularly in the 1,5-position, should proceed by an intramolecular chain mechanism. The high rate of hydrochlorination is considered by the authors to be one of the arguments supporting an intramolecular chain mechanism for the addition of hydrogen chloride to polyisoprene. In this they do not admit the possibility of electronic interaction of double bonds separated by three C–C bonds. We assume that just such interaction of double bonds in the 1,5 position creates the conditions for the development of hydrochlorination by a chain intramolecular mechanism. The greater activity of inner double bonds towards hydrogen chloride compared with vinyl bonds[37,50] is interesting.

The hydrochlorination of polyisoprenes in latex has been studied in detail[47,49,51–53]. At normal pressure the reaction rate in very low, owing to the low rate of diffusion of hydrogen chloride in the latex globules. Raising the pressure to 2 atm increases the reaction rate tenfold. Here the concentration of hydrogen chloride in the latex is increased by only a few per cent. The reaction has a negative temperature coefficient. The hydrochlorination of natural *cis*-polyisoprene in latex reaches 98–99%, and cyclisation is absent.

The addition of hydrogen bromide to natural *cis*-polyisoprene in the presence of peroxide takes place by a radical mechanism with the formation of a secondary bromide[37]. A kinetic analysis of the hydrobromination products showed the high activity of bromine in the addition products characteristic of tertiary bromides. Tuot[54] explains this by the influence of the methyl group situated in the $\alpha$ position to the secondary bromine. With secondary chlorides such an influence of the methyl group on the reactivity of the chlorine is not observed.

### 3. Hydrogenation

Hydrogenation occupies a special place in the chemistry of diene polymers. In the classical studies of the hydrogenation of natural rubber, made by Staudinger[55] and Pummerer[56], a series of important observations were made and the concept of macromolecules was formulated. Recently the hydrogenation of polyisoprene has been studied by Yakubchik and coworkers[57]. Natural and synthetic *cis*-polyisoprenes at 0.5% concentration in decalin are hydrogenated on a nickel catalyst at 80–140°C and a pressure of 80–100 atm, in the presence of 1% antioxidant. Synthetic polyisoprene, which has a lower molecular weight, is hydrogenated more readily; in the opinion of the authors this is due to the greater mobility of segments of its macromolecules as compared with natural *cis*-polyisoprene. The extent of the reaction increases with the temperature and with increase in the amount of catalyst. The maximal extent of the reaction is ~ 80% saturation of the double bonds. Spectrochemical analysis showed the absence of *trans*-links in the hydrogenation product. The refractive index

decreases linearly with the extent of reaction, on the basis of which the authors conclude that there is no cyclisation. However, this conclusion requires additional proof, since a decrease in refractive index due to decrease in the number of double bonds can exceed its increase due to cyclisation.

Bateman and coworkers[58] noted a diminished reactivity for natural *cis*-polyisoprene compared with the low-molecular model alkenes in the hydrogenation. Evidently this is connected with the reduction in electron density of the double bonds in 1,5-polyene systems due to the interaction of the double bonds. As already noted above, the interaction of double bonds in such systems creates conditions for the development of reactions of 1,5-polyenes by an intramolecular chain mechanism.

The hydrogenation of polybutadiene has received great attention. Jones[59] studied its hydrogenation on a nickel catalyst at 140–180°C; the quantity of catalyst employed is the determining factor in the reaction. The introduction of all the catalyst at once is more effective than its introduction in portions. The temperature has a marked effect on the extent of the reaction. Raising the temperature from 140° to 180°C reduces the unsaturation of the product from 34.6% to 9.5%.

Degradation of the polymer does not take place in the hydrogenation. According to infrared spectroscopy, the vinyl bonds are hydrogenated somewhat more rapidly than the inner double bonds, but at a residual unsaturation of 20%, vinyl groups are still present.

Yakubchik and coworkers[60,61] studied the hydrogenation of a polybutadiene with 57% 1,4-structure in heptane and hexane at 20°C on a nickel catalyst at a pressure of 1 atm. Varying the concentration of the solution within the range 0.2–0.8% did not affect the reaction. The reaction was finished in 20–30 min when its extent was ~ 60%. Apparently cyclisation was absent, as was shown by the diminished refractive index. The relative viscosity was somewhat reduced, owing to a change in the configuration of the macromolecules, but the molecular weight remained constant. For hydrogenation in iso-octane at 60–140°C the reaction rate was almost independent of temperature.

The hydrogenation of *cis*-polybutadiene (unsaturation 95% of theoretical, 5% *trans*-1,4-units, 6% vinyl bonds) was investigated in decalin in the presence of 1% Neozon D, on palladium, platinum, and nickel catalysts[62–64]. Whereas the hydrogenation of low-molecular alkenes proceeds at constant rate up to 50% conversion, the rate of hydrogenation of the macromolecules of *cis*-polybutadiene drops during the course of the reaction owing to the marked change in the rigidity of the chain, accompanied by a sharp rise in viscosity on going from a polydiene with a *cis*-configuration to a saturated polyethylene. Non-regular polybutadiene does not exhibit the flexibility of *cis*-polybutadiene, therefore its hydrogenation is not accompanied by so significant an increase in viscosity.

In the hydrogenation of an unfractionated specimen of polybutadiene a mixture of macromolecules with different degrees of unsaturation is formed[65–67]. This non-homogeneity of the hydrogenation products may be due both to the heterogenic nature of the reaction, the influence of the molecular weight of the polymer, and also to the interaction of the double bonds in the 1,5-polyene systems.

Fractionation of the products of the incomplete hydrogenation of sodium butadiene rubber on a palladium catalyst leads to the production of a fraction with a marked difference in unsaturation (see Table)[66,67].

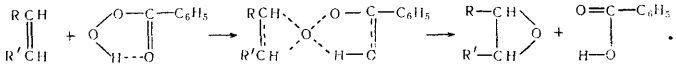
Polybutadiene can also be hydrogenated under homogeneous conditions in the presence of a soluble catalytic system of the Ziegler type[68,69]. The tri-isobutylaluminium–isopropyl titanate system can be used as the catalyst. The hydrogenation is effected in an autoclave at a pressure of 2–5 atm, 20–70°C, for 2–4 h. The ratio of the metal in the organometallic component to the transition metal is varied from 3 : 1 to 10 : 1.

As compared with the heterogeneous reaction, homogeneous hydrogenation permits a marked decrease in the amount of catalyst in the system, a reduction in the temperature and pressure, and there is less destruction of the polymer. Nothing has been published about the fractionation of the products of incomplete hydrogenation under homogeneous conditions.

## 4. Reaction with Perbenzoic Acid

The reaction of unsaturated compounds with perbenzoic acid was studied in detail by Prilezhaev[70–72]. It was found that the rate of reaction depends on the position and nature of the substituent at the double bond. The main reaction path yields epoxy-groups in an amount equivalent to the benzoic acid formed.

Apparently this reaction proceeds by a molecular mechanism as a result of the direct addition of oxygen at the site of the double bond[73]:



Chloroform and chlorobenzene are usually employed as solvents for carrying out reactions with diene polymers[73–80]. The reaction rate is increased fivefold on going from 6° to 24°C, but with rise in temperature side-reactions begin to occur.

Electronegative oxygen-containing groups (ether, carboxyl, aldehyde) at a double bond retard the reaction, alkyl groups accelerate the addition of perbenzoic acid. The difference in the rates of reaction of *cis*- and *trans*-double bonds is comparatively small. The rate of reaction of terminal and vinyl double bonds is less than the rate of reaction of the internal double bonds. The last fact forms the basis of a kinetic method of determining the structure of diene polymers developed by Dogadkin and Dobromyslova[75].

TABLE. Fractionation of the products of the hydrogenation of sodium butadiene rubber in the pentane–dioxan system

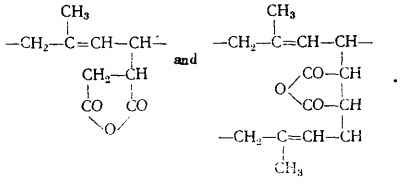
| Specimen fractionated | Fraction No. | Weight fraction, % | Unsaturation, % |
|---|---|---|---|
| Hydropolybutadiene with 42% unsaturation | 1 | 22.3 | 1.0 |
| | 2 | 18.6 | 1.5 |
| | 3 | 3.0 | 2.6 |
| | 4 | 29.4 | 66.0 |
| | 5 | 26.8 | 77.2 |
| Hydropolybutadiene with 24% unsaturation | 1 | 50.0 | 1.0 |
| | 2 | 7.0 | 1.6 |
| | 3 | 10.6 | 1.0 |
| | 4 | 5.4 | 4.0 |
| | 5 | 27.0 | 66.0 |

## III. REACTIONS INVOLVING THE PARTICIPATION OF DOUBLE AND ALLYL BONDS

### 1. Reaction with Ethylenic Monomers

The reaction of maleic anhydride with natural polyisoprene was first examined by Bacon and Farmer[81]. The reaction was carried out in the presence of benzoyl peroxide at 100°C. The extent of the reaction is proportional to the concentration of the peroxide and the remaining concentration of maleic anhydride. The best solvents for carrying out the reaction are carbon tetrachloride, decalin, and cyclohexane. In benzene, toluene, and xylene reaction is slight. At polymer concentrations $> 3\%$ or at a peroxide concentration $> 1\%$, calculated on the rubber, gel formation takes place. Temperature has little effect on the reaction. The authors assume that each molecule of the anhydride is attached to two double bonds of the polyisoprene, neighbours in a single macromolecule, adjacent in two macromolecules, or adjacent in a single macromolecule.

Later, Farmer proposed a different reaction mechanism with participation of $\alpha$-methylene groups[86]. The double bonds do not participate in the reaction. The addition products are represented by the formulae:




Delalande[82-84] investigated the reaction of polyisoprenes with ethylene monomers under the conditions of thorough purification of the polymer and complete exclusion of oxygen from the reaction medium. *N*-methylmaleimide was used instead of maleic anhydride, which allowed the extent of the reaction to be determined from the proportion of bound nitrogen in the polymer. *p*-Bromobenzoyl peroxide was used instead of benzoyl peroxide, and its addition was determined from the amount of bromine in the reaction products. The reaction was carried out at 60–130°C. At higher reaction temperatures less gel was formed. At a peroxide concentrations $> 3\%$, gel formation was observed at any temperatures.

With increase in the concentration of the imide and peroxide the extent of the reaction increases. It was found that half the peroxide radicals add to the polyisoprene, the other half form an acid.

The reaction takes place in two stages. In the first stage of the reaction at 130°C there is a rapid addition of the imide and peroxide, then follows the second stage—the addition of the imide without the peroxide. The rate of the second stage is less by a factor of 200. Reducing the temperature from 130° to 60°C cuts the reaction rate by a factor of 130.

In addition to the kinetics of addition, the change in the degree of unsaturation of the polyisoprene in the reaction was studied by an iodometric method. The decrease in the unsaturated nature is always less than theoretical (assuming the imide was added to the double bond) and correlates better with the addition of peroxide radicals. The reaction proceeds according to the following scheme. Initially the peroxide decomposes into radicals:

$$AA \rightleftarrows 2A^* .$$

Then a peroxide radical detaches an $\alpha$-methylene hydrogen of the polyisoprene

$$A^* + RH \rightarrow AH + R^* .$$

The macroradical formed reacts with the double bond of the imide:

$$R^* + E \rightarrow RE^* .$$

The macroradical which is formed detaches an $\alpha$-methylene hydrogen from another polyisoprene molecule, etc.:

$$RE^* + RH \rightarrow REH + R^* .$$

Kinetic studies at 170°C in the absence of peroxide were carried out with the aim of explaining the mechanism of the slow stage of the reaction[84]. Gel formation is not observed at a concentration of polyisoprene in the solution up to 10%. At 170°C the amount of imide attached is seven times that at 110°C. The rate and extent of the thermal reaction increase with the initial concentrations of imide and polyisoprene.

The change in the unsaturation of the polymer during the thermal reaction was determined iodometrically and bromometrically. The values obtained by the second method were lower by a factor of two. In both instances the decrease in unsaturation is significantly less than theoretical (addition of imide at the double bond), which shows that the reaction proceeds by substitution. The considerably greater yield of double bonds in the iodometric determination is evidently connected with the fact that the bromine atom adds more readily at the double bond whereas the larger iodine atom is hindered by the imide moiety attached directly to the double bond. The small real change in unsaturation is probably due to cyclisation of the polyisoprene.

Delalande proposes the following mechanism for the thermal reaction of *N*-methylmaleimide with polyisoprene. Initially the double bond of the imide is opened, with the formation of a biradical:

$$E \rightarrow E^{**} .$$

The biradical detaches an $\alpha$-methylene hydrogen from a polyisoprene molecule:

$$E^{**} + RH \rightarrow^* EH + R^* .$$

The macroradical which is formed adds the imide at the double bond:

$$R^* + E \rightarrow RE^* .$$

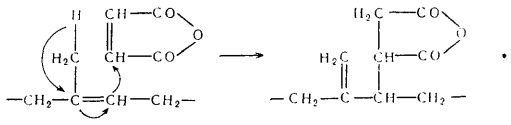
The re-formed macroradical reacts with the following polyisoprene molecule:

$$RE^* + RH \rightarrow REH + R^* .$$

Pinazzi and coworkers[85] and de Merlier and Le Bras[86] cast doubt on the radical nature of the thermal reaction, since thiophenol, which is a strong acceptor of radicals, has no effect on the thermal reaction although it retards the radical reaction which takes place in the presence of peroxide.

The presence of maleic anhydride was observed spectroscopically in the products of its reaction with polyisoprene in the presence of initiators[85]. Saturation of the double

bonds of polyisoprene or their isomerisation is not observed. In the thermal reaction (without initiator) the unsaturation of the polyisoprene does not alter and the reaction proceeds according to the scheme:



The NMR studies confirm the displacement of the double bond.

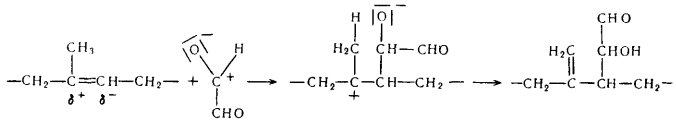
The more readily an ethylene monomer is polymerised, the greater the amount of graft polymer formed in its reaction with diene polymers. The ethylenic monomers with diminished electronic density of the double bond are readily added to *cis*-polyisoprene (maleic anhydride, γ-crotonolactone, *N*-methylmaleimide, fumaric and maleic acids, *p*-benzoquinone, acrylonitrile, chloromaleic anhydride) when there is no steric hindrance (fumarodinitrile, vinylidene chloride, etc.).

Monomers with enhanced electron density at the double bond (styrene, allyl alcohol) or with normal electron density (cyclohexene, indene) do not react with *cis*-polyisoprene.

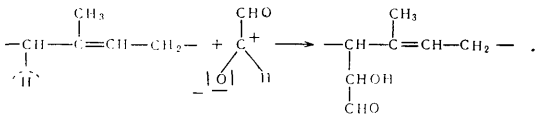
## 2. Reaction with Aldehydes

Pinazzi and Pautrat[87,88,91] investigated the reaction of *cis*-polyisoprene with glyoxal in xylene, under conditions where oxygen was thoroughly excluded from the reaction medium. The reaction was carried out at 25–180°C and the extent of the reaction was estimated from the oxygen content of the product. The reaction of glyoxal with polyisoprene is accompanied by a considerable gel formation, especially at low temperatures. At 180°C a soluble product can be obtained if the amount of glyoxal does not exceed 40 mole %, calculated on the polymer.

Usually, 24–32 moles glyoxal are added per 100 isoprene units. Examination of the reaction products by infrared spectroscopy and chemical analysis showed the presence of carbonyl and hydroxyl groups. The authors propose the following reaction mechanism:



and also assume that reaction can occur by the scheme:



The products of the reaction of glyoxal with polyisoprene are not homogeneous: unreacted polyisoprene could be extracted from the reaction medium; the amount extracted increased with decrease in temperature.

The reaction of natural *cis*-polyisoprene with chloral[89–91] has been investigated in solution in cyclohexane and decalin, free from peroxides. The reaction was carried out in an inert atmosphere (pure nitrogen) in the presence of 1–3% catalyst ($AlCl_3$, $BF_3$), calculated on the polyisoprene, at a polymer concentration in the solution of 2%. The product was fractionated in a methanol–chloroform mixture. For the main fraction, the concentration of combined chlorine gave the number of added molecules of chloral per 100 polyisoprene units ($n$). The reaction temperature was varied between 25° and 200°C and the excess of chloral from 0 to 1000%.

In the absence of a catalyst the reaction did not proceed far ($n = 3$) and was almost independent of temperature. In the range 25–180°C boron trifluoride is the more efficient catalyst; in the range 180–200°C, aluminium chloride is better. The catalyst efficiency increases with the temperature.

Increasing the excess of chloral to 300% leads to an increased extent of reaction, but a further increase has hardly any effect on it. The reaction of chloral with polyisoprene is accompanied by gel formation, the intensity of which depends on the type of catalyst (greatest gel formation on using $HgCl_2$, least with $AlCl_3$).

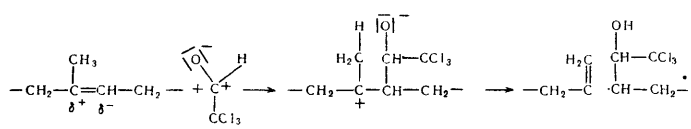
The effect of radical acceptors on the extent of reaction was investigated. The introduction of 3% thiophenol, *p*-benzoquinone, nitrobenzene, or sodium diethyldithiocarbamate had hardly any effect on the reaction of chloral with polyisoprene. To show whether a radical mechanism was possible, the reaction of chloral with polyisoprene in the absence of catalysts was studied. The initiators used were peroxides, azo-compounds, disulphides, and ultraviolet irradiation; all were ineffective.

The maximal addition ($n = 22$) was obtained by carrying out the reaction in cyclohexane at 180°C with aluminium chloride (3%) and a 300% excess of chloral. In the absence of a solvent at 180°C the reaction proceeds to $n = 5.5$. With thorough purification of the *cis*-polyisoprene the same results are obtained as for natural *cis*-polyisoprene. On carrying out the reaction with butyl rubber (3.5% isoprene) more than half of the double bonds react with the chloral. The extent of the reaction of *cis*-polybutadiene with chloral is very slight ($n = 1.5$).

Infrared analysis of the products of the addition of chloral to *cis*-polyisoprene showed the presence of hydroxyl groups (3300–3500 $cm^{-1}$) and chlorine (570, 620, 680, 730, and 1080 $cm^{-1}$), that is, the side chain has the structure $-CHOH-CCl_3$.

The characteristic frequencies of the cis-1,4-structure are weakened. The broadening of the 1640 $cm^{-1}$ peak and the appearance of a band at 860 $cm^{-1}$ show the formation of vinyldiene double bonds. The presence of a $-CHOH-CCl_3$ group has also been shown by chemical methods (reaction with sodium, phenyl-lithium, acetyl chloride, and alcoholic solution of potassium hydroxide). The appearance of absorption bands at 770 and 1040 $cm^{-1}$ and also the decrease in the viscosity of the polymer during the reaction shows that cyclisation takes place. There is little cyclisation in the presence of aluminium chloride and extremely little when boron trifluoride is used.

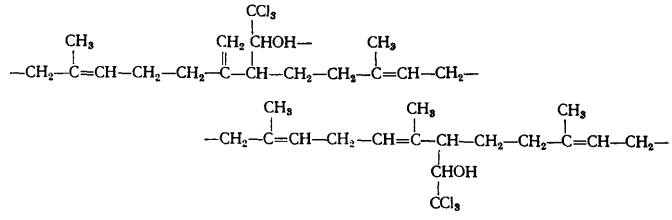
The addition of chloral proceeds at random along the chain. The probable reaction mechanism is:



The reaction mechanism for *cis*-polybutadiene is different. Here the group added is $-CCl_2-CHO$, as is shown by the appearance in the spectrum of a band at 1780 $cm^{-1}$,

characteristic for the carbonyl group, and the absence of the absorption band for hydroxyl.

The different reaction mechanisms for polyisoprene and polybutadiene with glyoxal can be explained as follows. The Prins reaction presumes the migration of a double bond with change of a methyl group into an exomethylene group or migration along the chain for polyisoprene.



and only along the chain for polybutadiene. The migration of one double bond along the chain reduces the effectiveness of the utilisation of the electrons in at least three isoprene units, since two double bonds prove to be in the 1,4-position, and two in the 1,6-position [13]. Hence the increase in the free energy of the system with the breakdown of the 1,5-sequence in the double bond alternation prevents the reaction with migration of a double bond.

### 3. Reaction with Molecular Chlorine

One of the most widely studied reactions of diene polymers is the chlorination of polyisoprenes and polybutadienes. Bloomfield's classical investigations allowed three main stages in the chlorination of natural rubber to be distinguished. In the first stage a molecule of chlorine reacts with an isoprene unit wholly by substitution:

$$C_{10}H_{16} + 2\,Cl_2 \rightarrow C_{10}H_{14}Cl_2\ (34.6\%\ Cl) + 2\,HCl\ .$$

In the second stage addition and substitution occur:

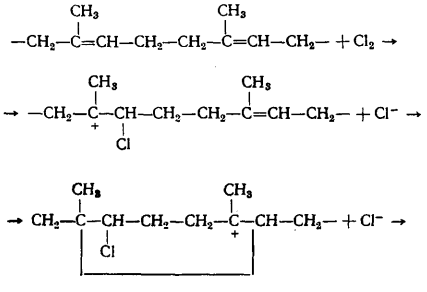
$$C_{10}H_{14}Cl_2 + 2\,Cl_2 \rightarrow C_{10}H_{13}Cl_5\ (57.2\%\ Cl) + HCl\ .$$

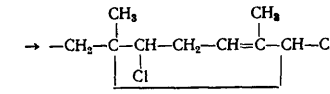
In the third stage there is only substitution:

$$C_{10}H_{13}Cl_5 + 2\,Cl_2 \rightarrow C_{10}H_{11}Cl_7\ (65.4\%\ Cl) + 2\,HCl\ .$$

The reaction was carried out in carbon tetrachloride in the temperature range −80° to +77°C, in the dark and in the light. The concentration of chlorine in the reaction products was determined by product analysis.

The chlorination of natural polyisoprene is accompanied a considerable drop in the viscosity of the solution (factor of 2–7) owing to the simultaneous occurrence of cyclisation (Bloomfield ascribes this effect to oxidation). At low temperatures cyclisation is insignificant and viscosity is reduced by a factor of 1.3. In the first stage of the reaction the unsaturation in the polymer diminishes (iodometric determination). Bloomfield suggests the following mechanism for cyclisation during chlorination:





Staudinger [40] suggests that cyclisation takes place with participation of the methyl groups.

Apart from cyclisation, the decrease in unsaturation shown iodometrically can be due to steric hindrance of the double bonds by neighbouring chlorine.

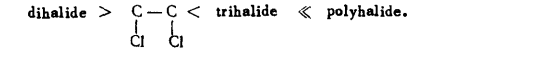
The chlorination of natural rubber does not take place by a radical mechanism since light, oxygen, peroxides, and antioxidants do not affect the reaction. When using sulphuryl chloride and phenyl dichloroiodate a radical mechanism of chlorination leads to the addition of chlorine at the double bond. An attempt was made to form radicals from molecular chlorine by irradiation and the introduction of peroxides. However, here also not addition of but substitution by chlorine was observed.

Kraus and Reynolds [93] investigated the chlorination of natural *cis*- and *trans*-synthetic polyisoprenes. The latter contained 90% *cis*- and *trans*-1,4-structures and 10% of the 1,2-structures. The properties of the chlorinated products were identical. The complete identity of natural *cis*- and *trans*-polyisoprenes on chlorination in the presence of antioxidant has been noted. The chlorination of synthetic polyisoprene proceeds similarly when the reaction takes place in the dark. In the light and in the presence of 0.3% oxygen (antioxidant absent) the addition to synthetic polyisoprene occurs even in the first stage of the reaction, and is increased on ultraviolet irradiation in the presence of 1% benzoyl peroxide.

Cyclisation is less pronounced in synthetic polyisoprene owing to the irregularity of the structure. In the early stages of the chlorination there is formation of one ring per three substitutions of chlorine. Until cyclisation has finished chlorine does not add to double bonds apart from those which are formed as a result of cyclisation and the vinyl bonds. In the presence of light and peroxides this rule is broken and addition proceeds at the expense of cyclisation.

A series of papers by Van Amerongen and coworkers [94-99] is devoted to the detailed explanation of the reaction mechanism of the chlorination of natural rubber. The structure of the products of the halogenation of rubber was determined by kinetic analysis, from the rate of reaction of the chloride with organic bases. Depending on the structure of the monochloride, the various types of chlorine are arranged in the following series of activity relative to aniline: allyl > tertiary ≫ primary > secondary ≫ ≫ vinyl.

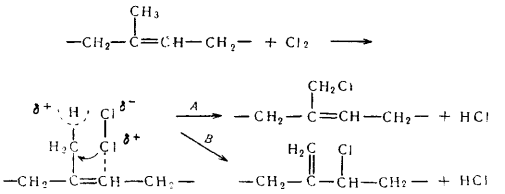
The order of reactivity of polyhalides has the following form:



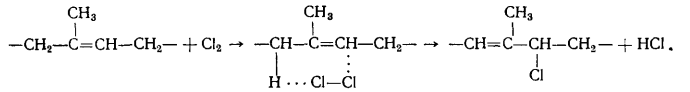
Kinetic investigations showed that the higher the chlorine content of the reaction product the more stable it is. The stability of the chlorination products depends on the total chlorine content and is independent of such experimental conditions as the presence of light or catalysts, temperature, chlorine pressure, or the effecting of the reaction in bulk or in solution with liquid or gaseous chlorine. This shows that the sequence of stages is retained during chlorination under different conditions: at first there is substitution then addition at the double bonds.

When there is less than 25% chlorine in the chloride of natural *cis*-polyisoprene, all the chlorine is allyl, as is shown by its high reactivity in the aniline experiment. In products with 65% chlorine the content of allyl chloride drops to 10%, owing to saturation of the double bonds. Further chlorination leads to an increase in the percentage of reactive chlorine due to the formation of the dichloride $-CCl_2-$.

Bloomfield and Van Amerongen and their coworkers adopt an ionic mechanism for the chlorination of diene polymers. The heterolytic breaking of a purely covalent bond seems improbable to us. The reaction of chlorine with a double bond by a molecular mechanism is more probable, as McNeill believes [100] for the chlorination of butyl rubber:



When an $\alpha$-methylene group participates in the reaction (for polybutadiene of 1,4-structure this is the only possibility) the double bond migrates along the macromolecular chain:



Whereas for the isolated double bonds of butyl rubber the migration of a double bond along a chain during chlorination does not encounter hindrance, a similar migration of one double bond in a 1,5-polyene chain should be accompanied by an increase in the free energy of the system owing to the breakdown of the condition of delocalisation of three double bonds, as was shown by the example of the reaction of polybutadiene or polyisoprene with chloral. However, when the intermediate complexes form successive links of a polymeric chain and the macromolecule or part of it changes into a collective excited state, forming a cooperative intermediate complex (CIC); the decomposition of such a CIC of any dimensions will be accompanied by the breakdown of interaction of only four double bonds (two at each end of the CIC). At the same time the gain in energy during the breakdown of the CIC to form addition products will increase additively with the inclusion in the CIC of each new link of the macromolecule and can considerably exceed the increase in energy of the system due to the breakdown of the conditions for the interaction of four double bonds. Hence a reaction of cooperative interaction can take place where a single addition with migration of a double bond along the chain is impossible.

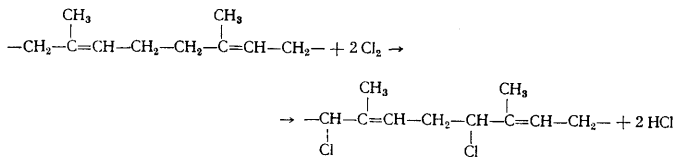
The formation of a CIC in reactions of diene polymers is favoured by the fact that the production of one intermediate complex facilitates the formation of analogous complexes by neighbouring links of a macromolecule owing to the increased reactivity of the double bonds in the 1,5-position relative to those which have reacted.

The cooperative mechanism for the first stage of the chlorination of polyisoprene provides an explanation for the fact that at this stage double bonds do not participate in cyclisation and addition [92,101]. If it be assumed that a CIC embraces the whole macromolecule it becomes understandable that double bonds can no longer participate in reactions up to the decomposition of the CIC with regeneration of double bonds in a new position.

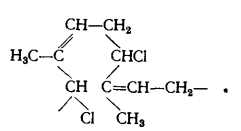
The products of incomplete chlorination of natural *cis*-polyisoprene (up to 30% bound chlorine) are non-homogeneous [94,101] even when chlorine dissolved in carbon tetrachloride is added dropwise to a solution of polyisoprene with vigorous stirring. In the chlorination products there is always a fraction with 31–33% chlorine [101]. With 34–35% chlorine the product is almost homogeneous, and the same is true for products with a higher content of chlorine [102]. According to Bloomfield 35% chlorine in the product corresponds to the end of the first stage of reaction, When the total chlorine in the product is $< 30\%$, 90–95% of this chlorine is reactive. Van Amerongen [94] explains the non-homogeneity of the product of incomplete chlorination by a high reaction rate in the first stage and by the existence of a zone of high concentration owing to the high viscosity of the solution. Trousier [101] considers that for a chlorine concentration of $< 34\%$ the chlorine which has been added favours the extension of the macromolecule, which facilitates further addition of chlorine to the same macromolecule. The viscosity results do not confirm this point of view. We assume that the reason for the products of the first stage of chlorination of polyisoprene being non-homogeneous is the cooperative intramolecular chain mechanism of the reaction.

An infrared analysis of the products of the chlorination of natural *cis*-polyisoprene [97,101,103–105] showed a weakening of the 3.4 $\mu$m (C–H bond) and 12 $\mu$m (*cis*-C=C) absorption bands until the latter disappeared completely during the chlorination. The 6 $\mu$m band ascribed to the C=C bond is constant up to 35% chlorine, then rises, but disappears at the end of chlorination. The intensity of the 6.9 $\mu$m band (C–H bond) remains constant. The 8 $\mu$m band (ring) appears at 35% chlorine and then rises. The 11 $\mu$m band (ring) appears during chlorination but its intensity falls for chlorine concentrations $> 35\%$.

Salomon and coworkers [97] ascribe the change in intensity of the 6 $\mu$m band and the appearance of the 11 $\mu$m band to the formation of vinyl bonds during chlorination. Allirot and Orsini [105] note a marked similarity between the spectra of the chlorides of polyisoprene and cyclohexane, and consider this to be confirmation of the cyclic structure of chlorinated polyisoprene. Trousier [101] considers that the changes in the spectrum are great only in the first stage of chlorination and ascribe them all to cyclisation. He represents the cyclisation mechanism as follows. After the first stage of chlorination:

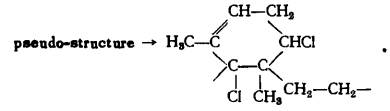


a pseudocyclic structure is formed:



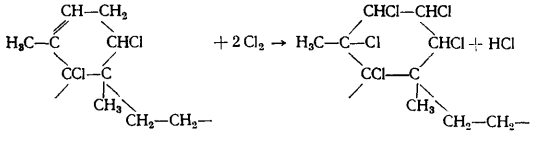
During this there are no significant changes in the spectrum, but a decrease in viscosity shows the contraction of

the macromolecular chains. Until the molecule is saturated with 35% Cl it does not cyclise. On reaching this threshold the individual macromolecules are cyclised according to the scheme:

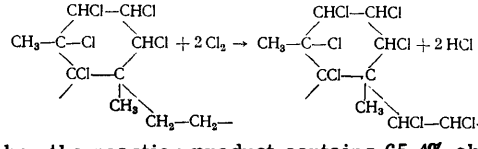


The results of the kinetic analysis confirm this picture: when the chlorine content of the reaction product is < 35% all the chlorine is allyl; on reaching 35% bound chlorine there is a sharp drop in the allyl chlorine content—its amount is cut by half. Further chlorination is accompanied by an increase in the reactive chlorine content; starting from 45% bound chlorine, the fraction of reactive chlorine drops monotonically.

The drop in viscosity stops after completion of the first stage of chlorination. Further chlorination proceeds under the condition that all the product was cyclised and there are no macromolecules with < 35% chlorine.



The products of this stage of chlorination are homogeneous. Substitution predominates over addition, as is shown by the increased content of allyl chlorine. The final stage of chlorination—the substitution



—ends when the reaction product contains 65.4% chlorine.

Ramakrishnan [106] studied the change in the unsaturation of natural *cis*-polyisoprene during chlorination by ozonation of the reaction products. A 4% solution of the polymer in carbon tetrachloride was saturated with gaseous chlorine at 2° and 78°C. With the aim of excluding the addition of hydrogen chloride formed in the substitution reaction, nitrogen was bubbled through the solution. The results obtained agree with the chlorination mechanism proposed by Trousier.

Canterino [107] notes the marked influence of the solvent on the chlorination of natural *cis*-polyisoprene. When the reaction is carried out in benzene hardly any cyclisation is observed—the double bonds do not disappear and the viscosity does not change. In the presence of phosphorus(III) chloride the cyclisation is greatly accelerated.

The chlorination of polybutadiene emulsion [107] proceeds somewhat more slowly and the product is more stable. When the reaction is carried out in carbon tetrachloride a cross-linked product is obtained; in benzene, chloroform, toluene, and tetrachloroethane, gel formation does not take place. The introduction into the reaction of iodine, phosphorus(III) chloride, phosphorus(V) chloride, or sulphuryl chloride prevents cross-linking, the phosphorus chlorides being the most effective in this respect. The chlorination products do not contain phosphorus. The substitution in polybutadiene is less pronounced than that in *cis*-polyisoprene and diminishes on going from carbon tetrachloride to benzene. The cyclisation occurs weakly in benzene, somewhat more in carbon tetrachloride, and is absent in both instances when phosphorus(III) chloride is used.

Van Amerongen [98] described the chlorination of natural and polychloroprene latex in strongly acid medium with an emulsifier. The latex concentration was 30–55% and the reaction was carried out at 15–90°C. Natural latex was chlorinated up to 60% combined chlorine in the reaction product, and the polychloroprene latex up to 48% combined chlorine. Within the limits given the temperature had hardly any effect on the rate or extent of the reaction.

## 4. Reaction with Bromine and Other Halogenating Agents

The quantitative addition of bromine at double bonds with the formation of a tetrabromide is used in gravimetric analysis [108–111]:

$$(C_{10}H_{16})_n + 2n Br_2 \rightarrow (C_{10}H_{15}Br_4)_n$$

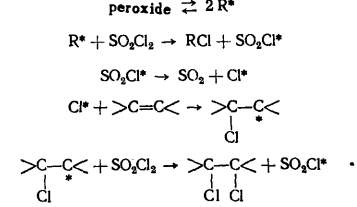
and in volumetric [112–114] methods of determining the unsaturation of diene polymers. The rate of bromination of the polyisoprenes increases with the temperature, but at temperatures above 0°C the addition of bromine is accompanied by substitutions and cyclisations [115–119]. The usual solvents employed for the reaction are benzene, chloroform, and carbon tetrachloride. Radiation accelerates the reaction but favours substitution. Substitution can be suppressed by use of a polar reagent (glacial acetic acid) [116].

The bromination of *cis*-polybutadiene was investigated at temperatures between 0° and −20°C in chloroform. Under these conditions there is only addition of bromine at the double bonds; cleavage, substitution, and cyclisation do not take place [120].

The products of the incomplete bromination of natural rubber and gutta-percha are not homogeneous [13, 121]. The bromination [13] was carried out in benzene (0.3% solution of polyisoprene), and the brominating solution (5% bromine in carbon tetrachloride) was introduced with cooling with ice and vigorous stirring. The amount of bromine corresponded to the theoretical for the desired degree of bromination.

To obtain homogeneous products from an incomplete bromination, various procedures were tried, mainly based on the introduction of a third component, but none of them gave positive results. Evidently the bromination does not obey statistical laws and takes place by the intramolecular chain mechanism considered above.

On reacting with polyisoprenes [96], sulphuryl chloride forms a dichloride when the polymer has been thoroughly purified; otherwise, substitution is observed. At high temperatures or in the presence of iodine, the sulphuryl chloride decomposes and the chlorination of the rubber under these conditions follows the usual path. At 40–60°C in the light and in the presence of a catalyst (pyridine), sulphuryl chloride is added at the double bonds. In the presence of initiators (ascaridole, benzoyl peroxide), the Kharasch reaction takes place:

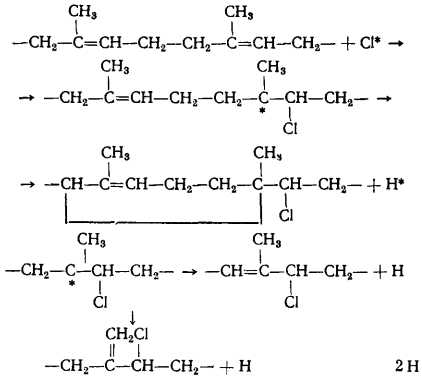


The reaction of sulphuryl chloride with natural *trans*-polyisoprene was investigated at 5–77°C in carbon tetrachloride. The presence of peroxide and ultraviolet radiation accelerates reaction. The content of reactive chlorine, capable of reaction with aniline, was always 5–7%. Little hydrogen chloride was formed. The temperature had little effect on the reaction. In the presence of inhibitors (hydroquinone, 2-naphthol) the reaction is slow and proceeds by substitution (~ 70% reactive chlorine), to a slight extent. Amino- and nitroso-compounds have a similar effect on the reaction.

The reaction of sulphuryl chloride with polyisoprenes is accompanied by gel formation, the extent of which increases with drop in temperature (when the rate of gel formation decreases), on irradiation, and in the presence of traces of water. Antioxidants do not affect the gel formation but nitrogen oxides hinder it. The introduction of 5% hydroperoxides, hydrogen iodide, iodine, or chlorine leads to a drop in the viscosity of the solution. Apparently hydrogen iodide deactivates radicals, leading to the cross-linking of the macromolecules; chlorine and peroxides break down the cross-linking.

In accordance with Bloomfield's results [122] phenyl dichloroiodate forms the dichloride almost exclusively when it reacts with natural *cis*-polyisoprene in the absence of oxygen. There is considerable substitution in the presence of inhibitors. Ramakrishnan [123], who studied the reaction products by use of ozonisation, considers that as well as the addition of chlorine at the double bonds, cyclisation, depolymerisation, decyclisation, and migration of double bonds with the release of a proton take place. The reaction mechanism is described by the following scheme:

$$RICl_2 \rightarrow RICl^* + Cl^*$$
$$RICl^* \rightarrow RI + Cl^*$$

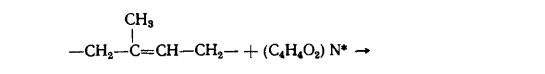


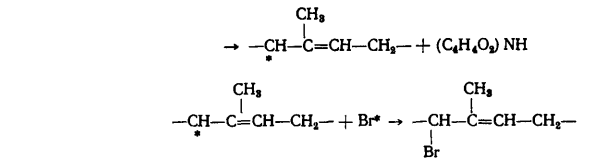
The migration of the double bond with release of a free proton is improbable. It was found that the release of hydrogen chloride in the individual stages of the reaction does not exceed 1–2%, and atmospheric oxygen has no effect on the reaction.

Bromination with *N*-bromosuccinimide [120] takes place through a change in the radical nature of the reaction. The first stage of the reaction is the decomposition of *N*-bromosuccinimide into radicals:

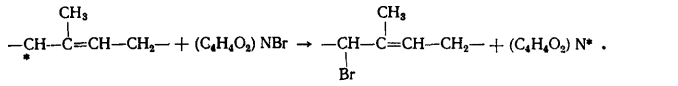
$$(C_4H_4O_2)NBr \rightarrow (C_4H_4O_2)N^* + Br^* .$$

The radicals formed react with the polyisoprene:





The macroradical can also react with the following molecule of *N*-bromosuccinimide:

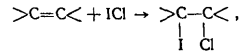


Cyclisation takes place simultaneously.

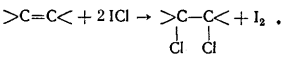
Iodine chloride adds quantitatively to polybutadiene when the reaction is carried out in a non-polar solvent at 25°C with an excess of iodine chloride [116]. In dichloroethane the addition is accompanied by substitution. For polyisoprene of non-regular structure the addition of iodine chloride is accompanied by substitution and cleavage. The hydrogen iodide liberated in the last two reactions reacts with iodine chloride to form molecular iodine:

$$HI + ICl \rightarrow HCl + I_2 .$$

The addition of chlorine iodide proceeds according to the scheme:



and not as follows



The reaction takes place by an ionic mechanism and initiators and inhibitors of radical reactions have no effect on it. The presence of alkyl groups at the double bond accelerate the addition, a halogen atom at the double bond retards the reaction. It is suggested that an internal double bond should react 2–4 times more rapidly than a vinyl group [119]. According to their activity in relation to iodine chloride, diene polymers form the following series: polyisoprene > polybutadiene > polychloroprene. When there are conjugated bonds the iodine chloride rapidly adds to the first bond and slowly to the second.

Iodine bromide adds to polybutadiene in carbon tetrachloride without release of hydrogen halide [124]. The formation of hydrogen iodide increases with the solvent used in the following order: chloroform–dichloroethane–tetrachloroethane. Ultraviolet irradiation assists substitution. The liberation of hydrogen iodide is much greater with polyisoprene.

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The above analysis of the reactions of diene polymers allows us to find characteristics for 1,5-polyene systems, consisting in the interaction of the double bonds, the reduction of their reactivity, and the possibility of development of the reactions of such systems according to an intramolecular chain mechanism. Such interaction of double bonds greatly complicates the solution of practical problems connected with the treatment and stabilisation of diene polymers. Thus for vulcanisation the development of reactions by an intramolecular chain mechanism should lead to

an extremely inefficient use of the vulcanising agent and to an undesirable modification of the polymeric chains which actually occurs during sulphur vulcanisation, especially in the absence of an accelerator. The autocatalytic nature of the oxidation of 1,5-polyenes and the accumulation of oxidation products in separate macromolecules [125] are also evidently connected with the interaction of the double bonds in these polymers. We suggest that detailed study of the possibility of developing the reactions of diene polymers by an intramolecular chain mechanism is now one of the most pressing problems of the chemistry of 1,5-polyenes.


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Lomonosov Moscow Institute of
Fine Chemical Technology