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ISOPRENE

From the time that isoprene was isolated from the pyrolysis products of natural rubber (1), scientific researchers have been attempting to reverse the process. In 1879, Bouchardat prepared a synthetic rubbery product by treating isoprene with hydrochloric acid (2). It was not until 1954–1955 that methods were found to prepare a high *cis*-polyisoprene which duplicates the structure of natural rubber. In one method (3, 4) a Ziegler-type catalyst of trialkylaluminum and titanium tetrachloride was used to polymerize isoprene in an air-free, moisture-free hydrocarbon solvent to an all *cis*-1,4-polyisoprene. A polyisoprene with 90% 1,4-units was synthesized with lithium catalysts as early as 1949 (5).

With the availability of polymerization catalysts, extensive efforts were devoted to developing economical processes for manufacture of isoprene. Several synthetic routes have been commercialized. With natural rubber as an alternative, the ultimate value of the polymer was more or less dictated by that market. The first commercial use of isoprene in the United States started in 1940. It was used as a minor comonomer with isobutylene for the preparation of butyl rubber. Polyisoprene was commercialized extensively in the 1960s (6). In the 1990s isoprene is used almost exclusively as a monomer for polymerization (see Elastomers, synthetic–polyisoprene).

The isoprene unit exists extensively in nature. It is found in terpenes, camphors, diterpenes (eg, abietic acid), vitamins A and K, chlorophyll, and other compounds isolated from animal and plant materials. The correct structural formula for isoprene was first proposed in 1884 (7).

1. Properties

Isoprene [78-79-5] (2-methyl-1,3-butadiene) is a colorless, volatile liquid that is soluble in most hydrocarbons but is practically insoluble in water. Isoprene forms binary azeotropes with water, methanol, methylamine, acetonitrile, methyl formate, bromoethane, ethyl alcohol, methyl sulfide, acetone, propylene oxide, ethyl formate, isopropyl nitrate, methylal (dimethoxymethane), ethyl ether, and *n*-pentane. Ternary azeotropes form with water–acetone, water–acetonitrile, and methyl formate–ethyl bromide (8). Typical properties of isoprene are listed in Table 1.

Many of the common properties of isoprene have been presented graphically (9). These include vapor pressure, heat of vaporization, liquid heat capacity, vapor heat capacity, liquid density, vapor viscosity, liquid viscosity, surface tension, and vapor thermal conductivity.

1.1. Conformation

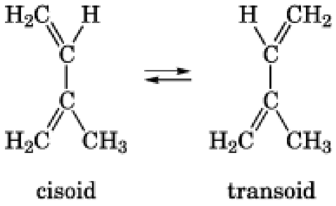
The exact conformation of the isoprene molecule is still in doubt. It is generally accepted that rotation is restricted around the central C—C single bond. Isoprene may be considered as an equilibrium of two conformations, namely a cisoid (*s-cis*) conformation in which both vinyl groups are located on the same side of the C—C bond, and a transoid (*s-trans*) one with the vinyl groups located on the opposite sides of the bond.

Table 1. Properties of Isoprene

Property	Value
mol wt	68.11
density of liquid, gm/cm^3 at 25°C	0.6759
freezing point, °C	−145.95
bp at 101.3 kPa,[a] °C	34.067
n_D^{30}	1.41524
flash point, °C	−48
autoignition, °C	220
dipole moment of liquid, C·m[b]	9.4×10^{-31}
heat of combustion at 25°C, kJ/mol[c]	146
heat of formation at 25°C, kJ/mol[c]	
liquid	49.4
gas	75.78
coefficient of expansion (−20.6 to 21.1 °C)	0.0016

[a] To convert kPa to atm, divide by 101.3.
[b] To convert C·m to debye, multiply by 2.997×10^{29}.
[c] To convert kJ to kcal, divide by 4.184.

The predominance of the trans-planar or nonplanar configuration has been supported by experimental data (10–14).



The energy required for a trans–cis change in conformation has been calculated to be 4.59 kJ/mol (1.10 kcal/mol) (14) and 6.28 kJ/mol (15). This difference is not considered sufficiently large to prevent easy interconversion (16), and is not great enough to provide a barrier to chemical reactions requiring the cis form, eg, in the Diels-Alder reaction of isoprene with maleic anhydride (14). The transoid geometry of butadiene is accepted as the more stable one in the ground state, but in the excited state, the cisoid and transoid forms are of nearly equal energy and of similar stability (17). Similar behavior is anticipated for isoprene. Conformational considerations are important in polymerization. Polymer structures with reference to the conformation of the monomer have been discussed (18–21).

2. Reactions

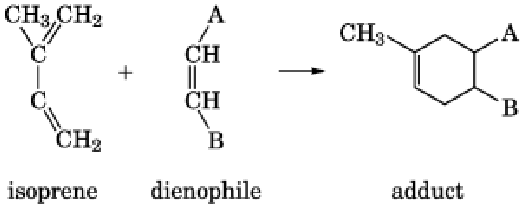
Isoprene is highly reactive both as a diene and through its allylic hydrogens, and its reactions are similar to those of butadiene (qv) (8). Apart from polymerization, the most widely investigated isoprene reactions are the formation of six-membered rings by the Diels-Alder reaction:

Table 2. Distribution of Isomers Produced by the Reaction of Isoprene with Unsymmetrical Dienophiles, $CH_2{=}CHX$

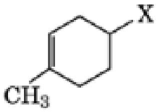
X	Temperature, °C	1,4-Analogue, %	Reference
$COCH_3$	25[a]	93	23
$COCH_3$	120	71	(23, 24)
CHO	25[a]	96	23
CHO	120	59	23
CHO	200[b]	64	25
$COOCH_3$	25–350	70	26
$COOCH_3$	25[b]	85	25
$COOCH_3$	120[b]	80	25
$COOCH_3$	200[b]	67	25
$COOCH_3$	400[b]	58	25
COOH	200[b]	65	25
C_6H_5	200	77	24
NO_2	150	79	24
OC_6H_5	250	75	(27, 28)

[a] In the presence of $SnCl_4{\cdot}5H_2O$.

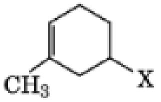
[b] In the presence of hydroquinone.



The reaction proceeds readily, depending on the nature of the dienophile, and normally no catalyst or inhibitor is effective. The substituents, A and B, in the adduct retain their configuration relative to the double bond originally present in the dienophile (22). Many materials having the general structure CH_2=CH—X react with isoprene to give mixtures of two isomers **(1)** and **(2)**.



(1)

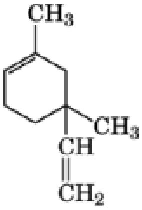


(2)

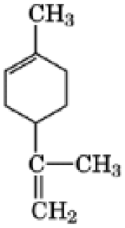
Generally, isomer **(1)**, the 1,4-analogue, predominates (Table 2). Bulkier substituent groups in the unsymmetrical dienophile favor the production of the 1,4-adduct. This is confirmed by work using dienophiles that contain two substituent groups; eg, CH2=C[CH(CH_3)$_2$]$COOC_2H_5$, in the reaction at 200°C in the presence of hydroquinone, gives 81% of the 1,4-analogue, whereas CH_2=C(CH_3)$COOCH_3$ gives only 72% of the 1,4-analogue (25).

Maleic anhydride has been used in many Diels-Alder reactions (29), and the kinetics of its reaction with isoprene have been taken as proof of the essentially transoid structure of isoprene monomer (30). The Diels-Alder reaction of isoprene with chloromaleic anhydride has been analyzed using gas chromatography (31). Reactions with other reactive hydrocarbons have been studied, eg, the reaction with cyclopentadiene yields 2-isopropenylbicyclo[2.2.1]hept-5-ene (32). Isoprene may function both as diene and dienophile in Diels-Alder reactions to form dimers.

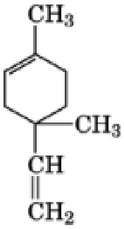
In the absence of air or peroxides, only cyclic dimers are formed in the thermal dimerization of isoprene (33). Six cyclic dimers are formed in good yields: four substituted cyclohexenes **(3–6)** and two dimethylcyclooctadienes **(7–8)**. The latter two are, of course, not Diels-Alder dimers. There is some evidence that the isoprene dimerization mechanism differs from the usual Diels-Alder route.



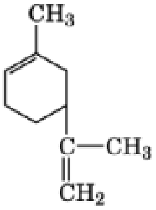
(3)
[*1611-21-8*]



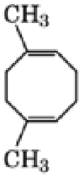
(4)
[*138-86-3*]



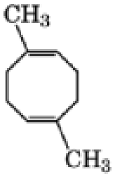
(5)
[*1743-61-9*]



(6)
[*38738-60-2*]



(7)
[*3760-13-2*]



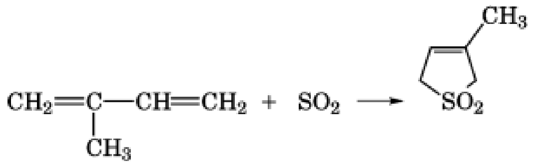
(8)
[*3760-14-3*]

The proportions of the various dimers depend on the reaction conditions. Dimers **(4)** and **(6)** constitute 57–80% of the products that are formed from 100–190°C. At 520°C, compounds **(3)** and **(4)** are the principal reaction products (34). The rate of dimer formation as a function of temperature ranges from 0.000017% isoprene dimerized per hour at 20°C to 0.25%/h at 100°C (35).

In the process of thermal dimerization at elevated temperatures, significant polymer is formed resulting in seriously decreased yields of dimer. Dinitrocresol has been shown to be one of the few effective inhibitors of this thermal polymerization. In the processing of C_5 streams, thermal dimerization to convert 1,3-cyclopentadiene to dicyclopentadiene is a common step. Isoprene undergoes significant dimerization and codimerization under the process conditions.

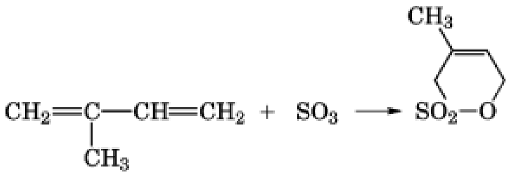
The dimerization of isoprene has been accomplished by methods other than heating. Thus isoprene has been dimerized by uv radiation in the presence of photosensitizers to give a complex mixture of cyclobutane, cyclohexene, and cyclooctadiene derivatives (36, 37). Sulfuric acid reportedly converts isoprene to linear and cyclic dimers (38). Ziegler-Natta coordination catalysts containing titanium (39, 40), nickel (41), and iron (42–44) dimerize isoprene at low temperatures. In most instances, the proportions of dimers differ from those obtained in thermal dimerizations, and linear trimers and higher homologues are also obtained in the reaction products.

Isoprene can form five-membered hydrocarbon rings (8). A five-membered, sulfur-containing ring is an intermediate in an isoprene purification reaction:

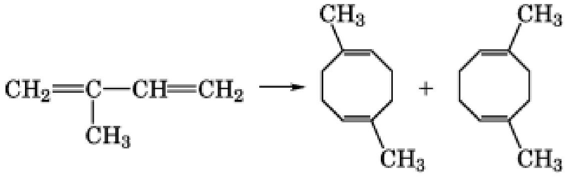


The solid sulfone can be recrystallized, and the isoprene can be regenerated by heating the purified sulfone (45, 46).

With SO_3–DMF (dimethylformamide) complex, a six-membered ring can form the delta sulfone (47):



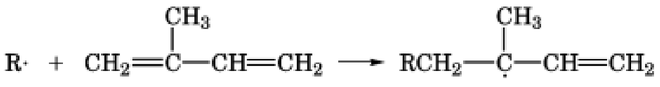
Eight-membered rings may be formed thermally or photochemically (see Photochemical technology). Excellent yields can be obtained with ferric acetylacetonate–triethylaluminum–dipyridyl (43).



Twelve-membered rings have been obtained using coordination catalysts. The *trans,trans,cis*-cyclododecatriene has been prepared with a tetrabutyl titanate–diethylaluminum chloride catalyst (48, 49) and with a chromium-based system (50). The *trans,trans,trans*-isomer has been prepared with a nickel system.

2.1. Free-Radical Reactions

Free radicals attack isoprene, and two competing mechanisms, at the double bond or involving C—H bonds, are postulated:



$$R\cdot + CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2 \longrightarrow RCH_2{-}\overset{\overset{CH_3}{|}}{\underset{\cdot}{C}}{-}CH{=}CH_2$$

The rates of these two reactions have been studied for the attack of trifluoromethyl (51) and methyl radicals (52) in isoprene that has been dissolved in 2,3-dimethylbutane and isooctane, respectively. The rate constants for the reactions with isoprene are much greater than those for the attack on the solvent. The ratio between the two rates for the attack of trifluoromethyl radicals varies from 1090 at 65°C to 233 at 180°C. For the corresponding reaction involving methyl radicals, the ratio is 2090 at 65°C.

The photosensitized dimerization of isoprene in the presence of benzil has been investigated. Mixtures of substituted cyclobutanes, cyclohexenes, and cyclooctadienes were formed and identified (53). The reaction is believed to proceed by formation of a reactive triplet intermediate. The energy for this triplet state presumably is obtained by interaction with the photoexcited benzil species. Under other conditions, photolysis results in the formation of a methylcyclobutene (54, 55).

The addition of aromatic and aliphatic thiols, RSH and ArSH, and a thioacetic acid to isoprene yields mainly the trans-1,4-adduct (56). The aromatic thiyl radicals, ArS·, add almost entirely to the first carbon atom; however, aliphatic thiyl radicals, RS, also add to the fourth C atom in significant amounts.

2.2. Halogens and Halogenated Compounds

The chlorination of isoprene in CCl_4 at -5 to $-10\ ^{\circ}C$, using an equimolar ratio of chlorine to isoprene, gives a mixture of 44% of 1,4-dichloro-2-methyl-2-butene and 14% of 3,4-dichloro-2-methyl-1-butene as addition products, along with 42% of the substitution product, 2-chloromethyl-1,3-butadiene (57). For the latter product, the reaction is an electrophilic substitution, and the carbon bearing the chlorine is not of the original methyl group in the isoprene molecule (58). At elevated temperatures (850°C) and in the vapor state, chlorine does not add but chlorinates the methyl in a free-radical substitution reaction. Thus a given reagent reacts by different mechanisms under different conditions.

Bromination of isoprene using Br_2 at $-5\ ^{\circ}C$ in chloroform yields only *trans*-1,4-dibromo-2-methyl-2-butene (59). Dry hydrogen chloride reacts with one-third excess of isoprene at $-15\ ^{\circ}C$ to form the 1,2-addition product, 2-chloro-2-methyl-3-butene (60). When an equimolar amount of HCl is used, the principal product is the 1,4-addition product, 1-chloro-3-methyl-2-butene (61). The mechanism of addition is essentially all 1,2 with a subsequent isomerization step which is catalyzed by HCl and is responsible for the formation of the 1,4-product (60). The 3,4-product, 3-bromo-2-methyl-1-butene, is obtained by the reaction of isoprene with 50% HBr in the presence of cuprous bromide (59). Isoprene reacts with the reactive halogen of 3-chlorocyclopentene (62).

The reaction of dihalocarbenes with isoprene yields exclusively the 1,2- (or 3,4-) addition product, eg, dichlorocarbene Cl_2C: and isoprene react to give 1,1-dichloro-2-methyl-2-vinylcyclopropane (63). The evidence for the presence of any 1,4 or much 3,4 addition is inconclusive (64). The cycloaddition reaction of 1,1-dichloro-2,2-difluoroethylene to isoprene yields 1,2- and 3,4-cycloaddition products in a ratio of 5.4:1 (65). The main product is 1,1-dichloro-2,2-difluoro-3-isopropenylcyclobutane, and the side product is 1,1-dichloro-2,2-difluoro-3-methyl-3-vinylcyclobutane. When the dichlorocarbene is generated from $CHCl_3$ plus aqueous base with a tertiary amine as a phase-transfer catalyst, the addition has a high selectivity that increases (for a series of diolefins) with a decrease in activity (66) (see Catalysis, phase-transfer). For isoprene, both mono-(1,2-) and diadducts (1,2- and 3,4-) could be obtained in various ratios depending on which amine is used.

Isoprene reacts with α-chloroalkyl ethers in the presence of $ZnCl_2$ in diethyl ether from 0–10°C. For example,α-chloromethyl methyl ether at 10°C gives a 6:1 ratio of the 1,4-adduct, (*E*)4-chloro-1-methoxy-2-methyl-2-butene, to the 1,2-adduct, 2-chloro-1-methoxy-2-methyl-3-butene. Other α-chloroalkyl ethers react in a similar manner to give predominately the 1,4-addition product. A wide variety of allylic chlorides and bromides and α-chloroethers and esters add primarily 1,4- to isoprene in the presence of acid catalysts (8).

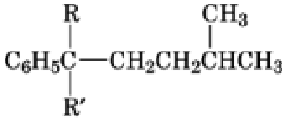
A telomerization reaction of isoprene can be carried out by treatment with 2-chloro-3-pentene, prepared by the addition of dry HCl to 1,3-pentadiene (67). An equimolar amount of isoprene in dichloromethane reacts with the 2-chloro-3-pentene at 10°C with stannic chloride as catalyst. 1-Chloro-3,5-dimethyl-2,6-octadiene is obtained in 80% yield by 1,4-addition.

Addition reactions between isoprene and tetrahalomethanes can be induced by peroxides, high energy ionizing radiation, or other radical-generating catalysts. In a radical reaction (68), carbon tetrachloride adds 1,4- to isoprene in 81–86% yield when catalyzed by chloro(triphenylphosphine)ruthenium(II). In the presence of cuprous chloride, dibromoacetonitrile also adds to isoprene (69). Isoprene reacts with carbon tetrabromide in carbon tetrachloride solvent on Co irradiation (70). Addition is induced using bromotrichloromethane in a 3:1 molar ratio to isoprene by x-irradiation (71). Only small amounts of the 1,2- and 4,3-addition products are obtained. The main reaction yields a mixture of ca 75% 1,4- and 25% 4,1-addition product.

2.3. Hydrocarbons

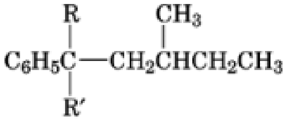
The reaction of isoprene with toluene, ethylbenzene, or isopropylbenzene is catalyzed by sodium or potassium (72). The reactions are carried out at 125°C in a pressure autoclave by adding the isoprene slowly to the alkylarene in which the alkali metal is dispersed along with a trace quantity of *o*-chlorotoluene which is used as a chain initiator. The products are chiefly monopentenylated in the side chain, and no information can be obtained on whether the addition is 1,4- or 1,2- since under these conditions the double bond migrates. The alkene products subsequently are reduced to alkanes by hydrogenation using 5% palladium on charcoal as catalyst.

With a sodium catalyst, the head product-to-tail product ratios are 2.77:1, 1.88:1, and 1.98:1 for toluene, ethylbenzene, and isopropylbenzene, respectively; corresponding ratios obtained using potassium are 3.04:1, 2.54:1, and 3.30:1.



$$C_6H_5\overset{R}{\underset{R'}{C}}-CH_2CH_2\overset{CH_3}{CH}CH_3$$

head product



$$C_6H_5\overset{R}{\underset{R'}{C}}-CH_2\overset{CH_3}{CH}CH_2CH_3$$

tail product

Alkylation of cyclohexane with isoprene can be carried out with alkyl radicals formed at 450°C and 20.3 MPa (200 atm) (73). 40% Pentenylcyclohexanes, 20% dipentenes (ie, substances having the general formula $C_{10}H_{16}$), and 40% higher boiling compounds are obtained using a 6.8 molar ratio of cyclohexane to isoprene and a space velocity of $2.5\ h^{-1}$. Of the pentenylcyclohexanes, the head and tail products are in equal amounts. Even stable radicals, eg, triphenylmethyl, add readily to isoprene (74). Olefins, eg, ethylene, propylene, and styrene, add to isoprene in the presence of coordination catalysts that are based on cobalt, nickel, or iron (8).

2.4. Other Compounds

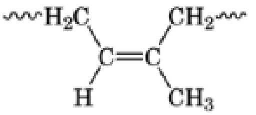
Primary and secondary amines add 1,4- to isoprene (75). For example, dimethylamine in benzene reacts with isoprene in the presence of sodium or potassium to form dimethyl(3-methyl-2-butenyl)amine. Similar results are obtained with diethylamine, pyrrolidine, and piperidine. Under the same conditions, aniline and *N*-methylaniline do not react. Isoprene reacts with phenol in the presence of aluminum phenoxide (76) or concentrated phosphoric acid (77) to give complex products.

At 165°C and in the presence of chloroplatinic acid as catalyst, isoprene reacts with trichlorosilane, methyldichlorosilane, ethyldichlorosilane, benzyldichlorosilane, and dibenzylchlorosilane (72). The addition is 1,4- with the substituted silane group attaching to the first carbon atom. Trimethylsilane does not react under these conditions. However, under similar conditions, heptamethylcyclotetrasiloxane reacts with isoprene by

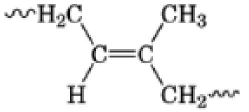
1,2-addition (78). Thiophene reacts with isoprene in the presence of phosphoric acid to give mainly 2-(3-methyl-2-butenyl)thiophene and some higher boiling compounds (79). Reactions of isoprene with Grignard reagents have been described (80, 81).

2.5. Polymerization

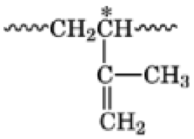
Isoprene polymerization can proceed by either 1,4- or 1,2-(vinyl)addition (see Elastomers, synthetic–polyisoprene). 1,4-Addition leads to two possible structures which differ in the configuration of the remaining double bond. Vinyl addition produces two other possible structures, depending on whether the 1,2- or the 3,4-double bond takes part in the polymerization reaction.



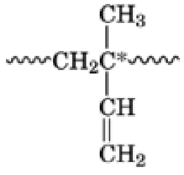
cis-1,4



trans-1,4



3,4-



1,2-

Any of the four monomer residues can be arranged in a polymer chain in either head-to-head, head-to-tail, or tail-to-tail configurations. Each of the two head-to-tail vinyl forms can exist as syndiotactic or isotactic structures because of the presence of an asymmetric carbon atom (marked with an asterisk) in the monomer unit. Of course, the random mix of syndiotactic and isotactic, ie, atactic structures also exists. Of these possible structures, only three are known, *cis*-1,4-polyisoprene is exemplified by natural rubber (hevea, guayule) and synthetic analogues (see Rubber, natural). Balata and gutta-percha are natural *trans*-1,4-polyisoprene, and there is synthetic trans as well. A high 3,4-polyisoprene has been prepared (82) and is amorphous, thus it is considered atactic. A crystalline 3,4-polyisoprene was reported in 1993 by Goodyear (83). Chinese scientists have reported similar results and the nmr of this 3,4-polyisoprene. Stereochemistry was not assigned due to the complex nature of the nmr spectrum. Because the polymer is crystalline and has a T_m of 120–130°C,

Table 3. Isoprene Specification for the Preparation of High *cis*-Polyisoprene[a]

Component	Specification, ppm[b]
isoprene	99.0 wt % (min)
isoprene dimer	0.2 wt %
olefins	1.0 wt %
acetylenes	30
allenes	100
carbonyls	30
sulfur	25
piperylene	100
cyclopentadiene	1.0
peroxides	3
acetonitrile	10

[a] Ref. 89.

[b] Unless otherwise noted.

the Goodyear investigators have assigned it the syndiotactic structure. There are still no reports of isotactic structure. None of the three possible 1,2-polyisoprenes has been synthesized. Many polymers with mixed cis, trans, or vinyl structures have been prepared. Several reports of mixed head-to-head and head-to-tail chains have appeared (84).

The physical properties of any polyisoprene depend not only on the microstructural features but also on macro features such as molecular weight, crystallinity, linearity or branching of the polymer chains, and degree of cross-linking. For a polymer to be capable of crystallization, it must have long sequences where the structure is completely stereoregular. These stereoregular sequences must be linear structures composed exclusively of 1,4-, 1,2-, or 3,4-isoprene units. If the units are 1,4- then they must be either all cis or all trans. If 1,2- or 3,4-units are involved, they must be either syndiotactic or isotactic. In all cases, the monomer units must be linked in the head-to-tail manner (85).

2.5.1. Al–Ti Catalyst for cis-1,4-Polyisoprene

Of the many catalysts that polymerize isoprene, four have attained commercial importance. One is a coordination catalyst based on an aluminum alkyl and a vanadium salt which produces *trans*-1,4-polyisoprene. A second is a lithium alkyl which produces 90% *cis*-1,4-polyisoprene. Very high (99%) *cis*-1,4-polyisoprene is produced with coordination catalysts consisting of a combination of titanium tetrachloride, $TiCl_4$, plus a trialkylaluminum, R_3Al, or a combination of $TiCl_4$ with an alane (aluminum hydride derivative) (86–88).

Table 3 provides typical specifications for isoprene that are suitable for Al–Ti polymerization (89). Traditional purification techniques including superfractionation and extractive distillation are used to provide an isoprene that is practically free of catalyst poisons. Acetylenes and 1,3-cyclopentadiene are the most difficult to remove, and distillation can be supplemented with chemical removal or partial hydrogenation. Generally speaking distillation is the preferred approach. Purity is not the main consideration because high quality polymer can be produced from monomer with relatively high levels of olefins and *n*-pentane. On the other hand, there must be less than 1 ppm of 1,3-cyclopentadiene.

2.5.2. Alkali Metal Catalysts

The polymerization of isoprene by alkali metal and organometallic compounds (90–92) (other than organolithium) is a heterogeneous reaction both in bulk and hydrocarbon solvents. A homogeneous reaction takes place only in the presence of highly polar solvents. A comprehensive evaluation of the influence of solvent and positive counterion on polymer structure has been given (93). Only lithium-based initiators in hydrocarbon lead to high cis-1,4 structures. A trend of decreasing cis structures is observed with an increase in solvent basicity. Alkali metals, other than lithium, generally yield polymers of mixed structures with low cis content. The ionic character of the propagating ion pair depends mainly on the metal counterion and the solvent type.

The first successful use of lithium metal for the preparation of a *cis*-1,4-polyisoprene was announced in 1955 (50); however, lithium metal catalysis was quickly phased out in favor of hydrocarbon soluble organolithium compounds. These initiators provide a homogeneous system with predictable results. Organolithium initiators are used commercially in the production of *cis*-1,4-polyisoprene, isoprene block polymers, and several other polymers.

The polymerization of isoprene in hydrocarbon solvents with organo(mono)lithium compounds, eg, butyllithium, is a homogeneous reaction. In the absence of inhibiting impurities, the reaction starts immediately and proceeds to essentially 100% conversion. At moderate temperatures, in hydrocarbon solvent and in the absence of compounds having an active hydrogen, there is practically no chain termination or transfer. This polymerization lends itself to the preparation of linear polymers of controllable molecular weights and narrow molecular weight distribution. Monomer of very high quality is necessary, but the polymerization is more tolerant of 1,3-cyclopentadiene than Ti–Al. Soluble organolithium compounds are the only initiators used in the preparation of block copolymers containing isoprene or butadiene. The failure of Ziegler-Natta catalysts to produce block copolymer resulted in the use of organolithium catalyst for the polymerization of diblock, triblock, and tetrablock copolymers of styrene and butadiene. The preparation of SIS (styrene isoprene styrene) and SISIS block polymers spurred new uses for isoprene monomer in the adhesive market. The introduction of block copolymers using 70–80% styrene and 20–30% isoprene or butadiene opened new film applications for these polymers.

2.5.3. Other Polymerization Systems

Extensive work during the 1970s on polymerization of butadiene in solution with soluble nickel complexes has led to general acceptance of the idea that catalyst sites involve a monometallic π-complex with a monomer (94, 95). A number of other coordination catalysts may be used to form high or very high *cis*-1,4-polyisoprene, eg, Zr salts or Mg alkyls (96), a cerium salt-based catalyst (97, 98), and uranium- and thorium-based catalysts (99). Uranium tetraalkoxide–aluminum alkyl–Lewis acid combinations can be used to form high *cis*-1,4-polybutadiene and high *cis*-1,4-polyisoprene (100). Several of the lanthanide and actinide rare-earth series make active catalysts which produce very high cis-1,4 structures from both monomers.

Another group of isoprene polymerization catalysts is based on alanes and $TiCl_4$. In place of alkyl aluminum, derivatives of AlH_3 (alanes) are used and react with $TiCl_4$ to produce an active catalyst for the polymerization of isoprene. These systems are unique because no organometallic compound is involved in producing the active species from $TiCl_4$. The substituted alanes are generally complexed with donor molecules of the Lewis base type, and they are liquids or solids that are soluble in aromatic solvents. The performance of catalysts prepared from $AlHCl_2O(C_2H_5)_2$ with $TiCl_4$ has been reported (101).

The preparation of high *trans*-1,4-polyisoprene with VCl_3 plus $(C_2H_5)_3Al$ catalyst has been described; it has been concluded that there are several species of active sites all of which give high *trans*-polyisoprene. Similar conclusions have been reached about varying catalyst species with vanadium salts during EPDM polymerizations. Several vanadium salts (VCl_3, $VOCl_3$, VCl_4) all yield *trans*-polyisoprene catalysts which might argue that the active catalyst is a single, lower valent species. *trans*-Polyisoprene also has been made with a η^3-2-propyl iodonickel catalyst (with no co-catalyst) and with tris(η^3-2-propenyl) chromium that is deposited on aluminosilicate (102).

3. Production

The usage of isoprene monomer is somewhat limited by price and availability. The historical large usage has been in the production of *cis*-1,4-polyisoprene which is similar to natural rubber. Although the price of natural rubber was expected to increase over time, it has remained relatively inexpensive since the 1960s. As a result, polyisoprene has been produced primarily where nonprice considerations were of utmost importance. The largest capacity has been and remains in the CIS (former USSR) region. Several plants around the world have been shut down, and the trend appears to continue downward. On the other hand the use of isoprene in block copolymers has grown rapidly. This growth has tended to offset some of the decline of *cis*-1,4-polyisoprene. In 1992 isoprene monomer was produced in Brazil, the Netherlands, Japan, CIS, Romania, and the United States. *cis*-1,4-Polyisoprene was produced in all locations except Brazil. World capacity for *cis*-1,4-polyisoprene is difficult to gauge. It is probably about 1,150,000 t, but the operating rate is probably well below that level. This compares with production in 1976 of 650,000 t. Because most producers of isoprene also produce polymer, accurate figures are not readily available.

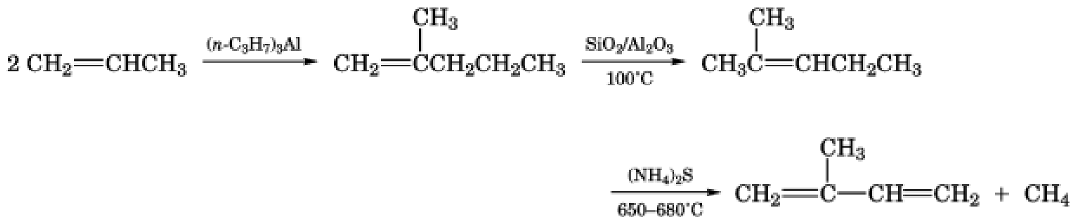
The principal route for production of isoprene monomer outside of the CIS is recovery from ethylene by-product C_5 streams. This route is most viable where ethylene is produced from naphtha or gas oil and where several ethylene plants are located in relatively close proximity to the isoprene plant. Although the yield of isoprene per mass of ethylene is quite low, there is enough ethylene produced to provide a large portion of demand. Because of the presence of *n*-pentane in these streams which azeotropes with isoprene, extractive distillation must be used to recover pure isoprene. Acetonitrile is the most common solvent, but dimethylformamide is also used commercially.

3.1. Synthesis

Because of the limited availability of by-product isoprene much effort has been devoted to synthesis of isoprene. Most routes tend to have marginal selectivity and require large amounts of energy. The choice of which route is preferable depends on availability and cost of raw materials and cost of energy. Several synthetic routes have been practiced commercially (103–108).

3.1.1. Propylene Dimer

The synthesis of isoprene from propylene (109, 110) is a three-step process. The propylene is dimerized to 2-methyl-1-pentene, which is then isomerized to 2-methyl-2-pentene in the vapor phase over silica alumina catalyst. The last step is the pyrolysis of 2-methyl-2-pentene in a cracking furnace in the presence of $(NH_4)_2S$ (111, 112). Isoprene is recovered from the resulting mixture by conventional distillation.

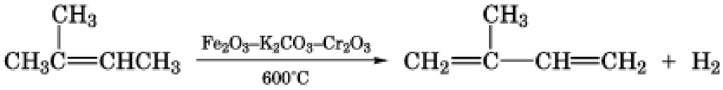


$$2\,CH_2{=}CHCH_3 \xrightarrow{(n\text{-}C_3H_7)_3Al} CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_2CH_3 \xrightarrow[100^\circ C]{SiO_2/Al_2O_3} CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_3$$

$$\xrightarrow[650\text{–}680^\circ C]{(NH_4)_2S} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + CH_4$$

3.1.2. Dehydrogenation of Tertiary Amylenes

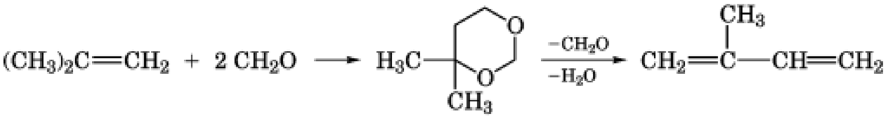
The starting material here is a C_5 fraction which is cut from catalytic cracking of petroleum. Two of the tertiary amylene isomers, 2-methyl-1-butene and 2-methyl-2-butene, are recovered in high purity by formation of methyl tertiary butyl ether and cracking of this to produce primarily 2-methyl-2-butene. The amylenes are mixed with steam and dehydrogenated over a catalyst. The crude isoprene can be purified by conventional or extractive distillation.



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 \xrightarrow[600^\circ C]{Fe_2O_3\text{–}K_2CO_3\text{–}Cr_2O_3} CH_2{=}\overset{CH_3}{\overset{|}{C}}\text{—}CH{=}CH_2 + H_2$$

3.1.3. *Isobutylene–Formaldehyde*

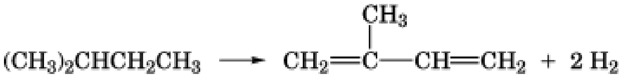
Isobutylene is condensed with formaldehyde at 95°C to give the principal product 4,4-dimethyl-*m*-dioxane. In the second step, the dioxane is decomposed in the presence of an acid catalyst to isoprene, formaldehyde, and water.



Much of the work with regard to this process was done by the French Petroleum Institute (113) and by the Kuraray Co. (108). In the CIS, a similar process which begins with crude C_5s was developed (114). A one-step process that begins with isobutylene and methanol has been disclosed (108, 115). This process is believed to have significant economic advantages over the original route.

3.1.4. *Isopentane Dehydrogenation*

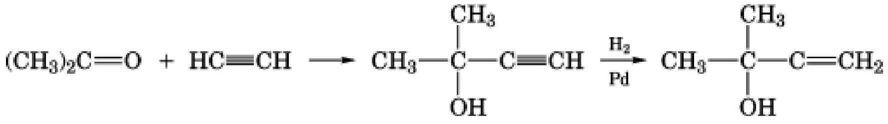
In isopentane dehydrogenation, which is used in the CIS, isopentane or a C_5 fraction from a catalytic cracker is dehydrogenated to isoprene (6):



$$(CH_3)_2CHCH_2CH_3 \longrightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}\text{—}CH{=}CH_2 + 2\,H_2$$

3.1.5. *Acetone–Acetylene*

A process based on acetone and acetylene (113–118) first was utilized in Germany. ANIC of Italy and Karbochem of South Africa have used this process to produce isoprene:



$$(CH_3)_2C{=}O + HC{\equiv}CH \longrightarrow CH_3\text{—}\underset{OH}{\overset{CH_3}{C}}\text{—}C{\equiv}CH \xrightarrow[Pd]{H_2} CH_3\text{—}\underset{OH}{\overset{CH_3}{C}}\text{—}C{=}CH_2$$

The ethynylation reaction takes place at 10–40°C and 2 MPa (20 atm) and liquid ammonia is the solvent. The methylbutynol is converted into methylbutenol by selective hydrogenation and then is dehydrated over alumina at 250–300°C. Polymerization-grade isoprene is obtained.

3.1.6. *Butene Hydroformylation*

A more recently developed process for the synthesis of isoprene is butene hydroformylation followed by dehydration. This process has not been practiced commercially, but processing steps are similar to commercial processes (119). 2-Butene is hydroformylated to 2-methylbutanol which is then dehydrated to isoprene.

4. Health and Safety

Isoprene is not known to present serious toxicological hazards in handling (2); however, like many chemicals studies are ongoing. A concentration of 2% isoprene in air does not narcotize mice but produces bronchial irritation. However, concentrations of 5% are fatal to mice. In humans, a one minute inhalation of 0.16 mg isoprene per liter air is mildly irritating to the mucous membranes of the eyes, nose, and upper respiratory passages (120). It was proposed that the limit of isoprene concentration on industrial sites be set at 0.04 mg/L air; it was also recommended that the maximum concentration of isoprene in water be set at 0.005 mg/L. The extent of toxic conditions and air pollution by isoprene in the manufacturing areas of synthetic rubber and their vicinity has been dealt with in several CIS publications (121–123). LC_{50} rat inhalation is $180\ g/m^2/2\ h$ for rats, and prolonged exposure may cause central nervous system depression.

Isoprene is classified by the ICC as a flammable liquid requiring a red label (124). Its flash point is –54°C with a lower explosive limit (LEL) of 1.5% and an upper explosive limit (UEL) of 8.9%. It forms dangerous peroxides on exposure to air in the absence of inhibitors. A solution having 17 wt % of peroxide does not detonate in a standard drop test. The polymeric peroxide residue that is obtained on evaporation does explode. The reaction of isoprene and oxygen is rapid, with 1% conversion of isoprene in about 3 h at 50°C; the product (125) is an alternating copolymer of oxygen and isoprene, with the repeating structure being $–(C_5H_9O_2)–$. The peroxide could serve as a source of initiation, which could lead to uncontrolled polymerization either homogeneously or as a popcorn growth, ie, peroxide polymer having the appearance of popcorn.

Because of the potential hazards on its exposure to oxygen, isoprene should be stored in an inert atmosphere (nitrogen) in the presence of at least 50 ppm of *t*-butylcatechol. Because the inhibitor is slowly consumed during storage, it is advisable to analyze the isoprene periodically and to add more inhibitor as needed. Before use it should be flash distilled to remove dimer and inhibitor. In industrial use, inhibitor is often removed by a caustic wash. A dangerous reaction of isoprene with ozone has been reported (126): when one gram of isoprene that was diluted with 50 mL of *n*-heptane was treated with ozone at -78°C, the resulting product exploded shortly after being removed from the cooling bath; however, the product of a similar reaction that was carried out at room temperature did not explode. On storage, isoprene forms cyclic dimers at a slow rate which is not affected by the presence of an inhibitor (35).

5. Economic Aspects and Applications

Isoprene pricing tends to vary considerably due to a fairly thin commercial market. Because isoprene raw materials are primarily petroleum based and synthesis or recovery is energy intensive, most pricing is indexed to petroleum and energy. For large-scale applications monomer production is in tandem with application production. Generally isoprene availability is less than butadiene, and the price is higher. Isoprene is used where the unique properties of the products can command a premium over butadiene. Almost all isoprene produced is used for the preparation of polymers or copolymers. *cis*-Polyisoprene is the largest application with SIS block polymers being a rapidly growing secondary application. Butyl rubber is a significant third application. Table 4 provides isoprene demand by use for 1985 and 1992, and provides synthetic polyisoprene consumption by region for the same years. Natural rubber consumption was 4.8–5.5 million tons per year over the same time period.

Table 4. World Isoprene Demand and Polyisoprene Consumption, 10^3 t

	1985	1992
Monomer use		
polyisoprene	1170	827
SIS	36	95
butyl rubber	31	25
other	4	10
Polymer use		
North America	45	60
Latin America	5	2
Western Europe	40	40
Middle East and Africa	20	0
Far East and Australia	60	45
Eastern Europe, CIS, and China	1000	680

BIBLIOGRAPHY

"Isoprene" in *ECT* 2nd ed., Vol. 12, pp. 64–83, by G. Holden and R. H. Mann, Shell Chemical Co.; in *ECT* 3rd ed., Vol. 13, pp. 818–837, by W. M. Saltman, The Goodyear Tire and Rubber Co.

Cited Publications

1. C. G. Williams, *Proc. Roy. Soc.* **10**, 516 (1860) *Phil. Trans.*, 241 (1860).
2. G. Bouchardat, *Comp. Rend.* **80**, 1117 (1879).
3. U.S. Pat. 3,144,743 (Dec. 17, 1963), (to Goodrich-Gulf Co.).
4. S. E. Horne and co-workers, *Ind. Eng. Chem.* **48**, 784 (1956).
5. F. W. Stavely and co-workers, *Ind. Eng. Chem.* **48**, 778 (1956).
6. I. V. Garmonov, paper No. 1, presented at the *International Symposium on Isoprene Rubber*, Moscow, Russia, 1972.
7. W. A. Tilden, *Chem. News* **46**, 120 (1882) W. A. Tilden, *J. Chem. Soc.* **45**, 410 (1884).
8. W. J. Bailey, in E. C. Leonard, ed., *Vinyl and Diene Monomers*, Part II, John Wiley & Sons, Inc., New York, 1971, Chapt. 5.
9. R. W. Gallant, *Hydrocarbon Process. Pet. Ref.* **46**(a), 155 (1967) *Physical Properties of Hydrocarbons*, Vol. **1**, Gulf Publishing Co., Houston, Tex., 1968, 157–166.
10. R. J. W. Le Feure and K. M. S. Sundaran, *J. Chem. Soc.*, 3547 (1963) R. J. W. Le Feure and K. M. S. Sundaran, *J. Chem. Soc.*, 3518 (1964).
11. L. V. Vilkov and I. N. Sadova, *Zh. Strukt. Khim.* **8**, 398 (1967).
12. G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.* **49**, 358 (1953) M. I. Batuev, A. S. Onischenko, A. D. Matveeva, and N. I. Aronova, *Dokl. Akad. Nauk. SSSR* **132**, 581 (1960) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.* **83**, 2885 (1961) H. Dodziuk, *J. Mol. Struct.* **20**, 317 (1974).
13. J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Am. Chem. Soc.* **82**, 5820 (1960).
14. D. A. C. Compton, W. O. George, and W. F. Maddams, *J. Chem. Soc. (Perkins II)* **14**, 1666 (1976).
15. S. Dzhessati, A. R. Kyazimova, V. I. Tyulin, and Yu. A. Pentin, *Vestn. Mosk, Univ. Khim.* **23**(5), 19 (1968).
16. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 291.
17. R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.* **88**, 943 (1966).
18. R. S. Stearns and L. E. Forman, *J. Polym. Sci.* **41**, 381 (1959).
19. I. Kuntz and A. Gerber, *J. Polym. Sci.* **42**, 299 (1960).
20. R. J. Orr, *J. Polym. Sci.* **58**, 843 (1962).
21. M. Szwarc, *J. Polym. Sci.* **40**, 583 (1959).
22. R. Adams, ed., *Organic Reactions*, Vol. **4**, John Wiley & Sons, Inc., New York, 1948, 60–173.

23. E. F. Lutz and G. M. Bailey, *J. Am. Chem. Soc.* **86**, 3899 (1964).
24. Yu. A. Titov and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1297 (1960).
25. I. N. Nazarov, Yu. A. Titov, and A. R. Kuznetsova, *Izv. Akad. Nauk SSSR Otd. Khim Nauk*, 1412 (1959).
26. H. E. Hennis, *J. Org. Chem.* **28**, 2570 (1963).
27. A. N. Volkov, A. V. Bogdanova, and M. F. Shostakovskii, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1280 (1962).
28. M. F. Shostakovskii, A. V. Bogdanova, and A. N. Volkov, *Izv. Akad. Nauk SSSR Otd. Khim Nauk*, 1284 (1962).
29. F. Bergmann and H. E. Eschinazi, *J. Am. Chem. Soc.* **65**, 1405 (1943).
30. D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.* **83**, 2885 (1961).
31. E. Gil-AV and Y. Herzberg-Minzly, *Proc. Chem. Soc.*, 316 (1961).
32. A. F. Plate and N. A. Belikova, *Zh. Obshch. Khim.* **30**, 3953 (1960).
33. A. S. Onishchenko, *Diene Synthesis*, Daniel Davey and Co., Inc., New York, 1964, 592–595.
34. Ya. M. Paushkin, A. G. Liakumovich, Yu. I. Michurov, R. B. Valitov and A. F. Lunin, *Tr. Mosk. Inst. Neftekhim. Gazov. Prom.* (72), 23 (1967).
35. *Storage and Handling of Liquefied Olefins and Diolefins*, Enjay Chemical Co., New York, 1962, p. 19.
36. G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.* **28**, 3297 (1963).
37. R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.* **87**, 3406 (1965).
38. B. S. Greensfelder and H. H. Voge, *Ind. Eng. Chem.* **37**, 983 (1945).
39. L. I. Zarharkin, *Dokl. Akad. Nauk SSSR* **131**, 1069 (1960).
40. H. Takahashi and M. Yagamuchi, *Osaka Kogyo Gijutsu Shikensho Kiho* **15**, 271 (1964).
41. L. I. Zakharkin and G. G. Zhigareva, *Izv. Akad. Nauk SSSR Serv. Khim.*, 168 (1964).
42. J. P. Candlin and W. H. Janes, *J. Chem. Soc. C*, 1856 (1968).
43. A. Misono, Y. Uchida, M. Hidai, and Y. Ohsawa, *Bull. Chem. Soc. Jpn.* **39**, 3425 (1966).
44. R. F. Heck, *Organotransition Metal Chemistry*, Academic Press, Inc., New York, 1974, p. 162.
45. R. L. Frank and R. P. Seven, in E. C. Horning, ed., *Organic Syntheses*, Collective Vol. **III**, John Wiley & Sons, Inc., New York, 1955, p. 499.
46. R. L. Frank, C. E. Adams, J. B. Blegen, R. Deanin, and P. V. Smith, *Ind. Eng. Chem.* **39**, 887 (1947).
47. T. Akiyama, M. Sugihara, T. Imagawa, and M. Kawanisi, *Bull. Chem. Soc. Jpn.* **51**, 1251 (1978).
48. H. Takahashi and M. Yamaguchi, *Osaka Kozyo Gijutsu Shikensho Kiho* **15**, 271 (1964).
49. Fr. Pat. 1,393,071 (Mar. 19, 1965), A. Carbonaro, A. Bonfardeci, and L. Porri (to Montecatini).
50. U.S. Pat, 3,429,940 (Feb. 25, 1969), F. T. Wadsworth (to Columbian Carbon Co.).
51. J. M. Pearson and M. Szwarc, *Trans. Faraday Soc.* **60**, 553 (1964).
52. A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc. (London)* **A251**, 394 (1959).
53. D. J. Trecker, R. L. Brandon, and J. P. Henry, *Chem. Ind. (London)*, 652 (1963).
54. K. J. Crowley, *Proc. Chem. Soc.* **334** (1962) *Tetrahedron* **21**, 1001 (1965).
55. R. Srinavasan, *J. Am. Chem. Soc.* **84**, 4141 (1962).
56. A. A. Oswald, K. Griesbaum, W. Thaler, and B. E. Hudson, Jr., *Am. Chem. Soc. Div. Petrol. Chem. Prepr.* **7**, 139 (1962).
57. M. J. Ljam, *The Addition of Halogens to Chloroprene and Isoprene*, Ph.D. dissertation, The University of Texas, Austin, 1961, p. 110.
58. E. G. E. Hawkins and M. D. Philpot, *J. Chem. Soc.*, 3204 (1962).
59. A. A. Petrov, *J. Gen. Chem. USSR* **13**, 741 (1943).
60. A. J. Ultee, *J. Chem. Soc.*, 530 (1948).
61. W. J. Jones and H. W. T. Cleorley, *J. Chem. Soc.*, 832 (1946).
62. V. N. Belov, V. K. Promonenkov, and A. B. Kamenskii, *Zh. Obshch. Khim.* **34**, 3432 (1964).
63. A. Ledwith and R. M. Bell, *Chem. Ind. (London)*, 459 (1959).
64. E. C. Herrick, *J. Org. Chem.* **24**, 139 (1959).
65. P. D. Bartlett, *J. Am. Chem. Soc.* **86**, 616 (1964).
66. Y. Kimura, I. Isagawa, and Y. Otsuji, *Chem. Lett.* (8), 951 (1977).
67. A. A. Petrov, N. A. Razumova, and M. L. Genusov, *Zh. Obshch. Khim.* **28**, 1128 (1958).
68. H. Matsumoto and co-workers, *Chem. Lett.* (1), 115 (1978).
69. Fr. Pat. 1,409,516 (Aug. 27, 1965), H. W. Moore, F. F. Rust, and H. S. Klein (to Shell).
70. G. Rabilloud and P. Traynard, *Compt. Rend.* **251**, 1505 (1960).
71. C. S. H. Chen and E. F. Hosterman, *J. Org. Chem.* **28**, 1585 (1963).

72. L. Shiihara, W. F. Hoskyns, and H. W. Post, *J. Org. Chem.* **26**, 4000 (1961).
73. L. Kh. Friedlin, N. M. Nazarivam, E. F. Litvin, and G. K. Gaivoronskaya, *Neftehimaya* **4**, 246 (1964).
74. J. B. Conant and H. W. Scherp, *J. Am. Chem. Soc.* **53**, 1941 (1931).
75. G. T. Martirosyan and E. A. Grigoryan, *Izv. Akad. Nauk Arm. SSR Khim. Nauk* **16**, 31 (1963).
76. K. C. Dewhirst and F. F. Rust, *J. Org. Chem.* **28**, 798 (1963).
77. A. R. Bader and W. C. Bean, *J. Am. Chem. Soc.* **80**, 3073 (1958).
78. K. A. Andrianov and co-workers, *Dokl. Akad. Nauk SSSR* **158**, 133 (1964).
79. H. Pines, B. Kvetinskas, J. A. Vesely, and E. Baclawski, *J. Am. Chem. Soc.* **73**, 5173 (1951).
80. M. S. Kharasch, R. D. Mulley, and W. Nudenberg, *J. Org. Chem.* **19**, 1477 (1954).
81. M. S. Kharasch, P. G. Holten, and W. Nudenberg, *J. Org. Chem.* **19**, 1600 (1954).
82. G. Natta, L. Porri, and A. Carbonaro, *Makromol. Chem.* **77**, 126 (1964).
83. W. L. Hsu and A. F. Halasa, *144th Meeting of the Rubber Division*, Paper No. 77, American Chemical Society, Washington, D.C., Oct. 1993.
84. E. Schoenberg, H. A. Marsh, S. J. Walters, and W. M. Saltman, *Rubber Chem. Tech.* **52**, 526 (1979).
85. G. Natta, *Mod. Plast.* **34**, 169 (1956).
86. C. T. Winchester, *Ind. Eng. Chem.* **51**, 19 (1959).
87. W. M. Saltman and E. Schoenberg, in J. R. Elliot, ed., *Macromolecular Syntheses*, Vol. **2**, John Wiley & Sons, Inc., New York, 1966, p. 50.
88. U.S. Pat. 2,851,505 (Sept. 9, 1958), S. M. Henke and V. N. Hurd (to Gulf Research and Development Co.) Brit. Pat. 837,908 (1962), (to Shell) U.S. Pat. 2,900,430 (Aug. 18, 1959), A. M. Henke and H. C. Stauffer (to Gulf Research and Development Co.).
89. R. Fowler and D. Barker, *Chem. Eng. (London)*, 322 (1971).
90. Brit. Pat. 24,790 (Oct. 25, 1911), F. E. Matthews and E. H. Strange.
91. C. H. Harries, *Ann.* **383**, 184 (1911).
92. Ger. Pats. 255,786 (Jan. 27, 1912), and 255,787 (Apr. 9, 1912), I. H. Labhartd (to BASF Badische Anilin).
93. R. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.* **40**, 73 (1959).
94. Ph. Teyssie and F. Dawans, in W. M. Saltman, ed., *The Stereo Rubbers*, Wiley-Interscience, New York, 1977, Chapt. 3.
95. B. A. Dolgoplosk, *Kinet. Katal.* **18**, 1146 (1977).
96. W. Cooper, in Ref. 94, 50–53.
97. U.S. Pat. 3,297,667 (Jan. 10, 1967), W. C. VonDohlon, T. P. Wilson, and E. G. Caflisch (to Union Carbide).
98. U.S. Pat. 3,541,063 (Nov. 17, 1970), M. C. Throckmorton and W. M. Saltman (to The Goodyear Tire and Rubber Co.).
99. U.S. Pat. 3,676,411 (July 11, 1972), M. C. Throckmorton and W. M. Saltman (to The Goodyear Tire and Rubber Co.).
100. M. Burzzone, A. Mazzei, and G. Giuliani, *Rubber Chem. Technol.* **47**, 1175 (1974).
101. W. Marconi, A. Mazzei, S. Cesca, and M. de Malde, *Chim. i Ind. (Milan)* **51**, 1084 (1969) W. Marconi, A. Mazzei, S. Cucinella, and M. de Malde, *Makromol. Chem.* **71**, 118, 134 (1964).
102. I. M. Kosheleva, N. N. Stefanovskya, and V. L. Shmonena, *Kautch. i Rezina.* **6**, 49 (1975).
103. M. J. Rhoad, *Proceedings of the 15th Annual Meeting*, International Institute of Synthetic Rubber Producers, Inc., Kyoto, Japan, 1974 *Rubber Ind. (London)* **9**(12), 68 (1975) *Rubber Plast. News*, 14 (Jan. 23, 1978).
104. S. K. Ogorohnikov and G. S. Idlis, *Isoprene Production*, Izdatelstvo Chimia, Leningrad, Russia, 1973.
105. *Isoprene*, Report No. 28, Stanford Research Institute, Menlo Park, Calif., 1967.
106. C. Capitani, *Rev. Gen. Caout. Plast.* **51**(4), 195 (1974).
107. A. Mitsutani, *Yuki Gosei Kagaku Kyokai Shi* **32**, 528 (1974).
108. A. Mitsutani and S. Kumano, *Chem. Econ. Eng. Rev.* **3**(2), 35 (1971).
109. V. J. Anhorn, K. J. Frech, J. J. Tazuma, P. H. Wise, and W. E. Morrow, *Chem. Eng. Prog.* **57**(5), 41 (1961).
110. V. J. Anhorn, K. J. Frech, G. S. Schaffel, and D. Brown, *Rubber Plast. Age* **42**, 1212 (1961).
111. H. J. Osterhof, *Rev. Gen. Caout. Plast.* **42**, 529 (1965).
112. U.S. Pat. 3,284,532 (Nov. 8, 1966), K. J. Frech (to The Goodyear Tire and Rubber Co.).
113. *Hydrocarbon Process. Pet. Ref.* **92**(11), 187 (1963) *Hydrocarbon Process.* **50**(11), 167 (1971).
114. *Hydrocarbon Process.* **50**(11), 168 (1971).
115. H. J. Peterson and J. O. Tucker, *Hydrocarbon Process.* **53**(7), 21 (1974).
116. *Hydrocarbon Process.* **50**(11), 170 (1971).
117. *Rubber World* **167**(2), 16 (1972).

118. M. DeMalde, *Chim. e Ind. (Milan)* **45**, 665 (1963).
119. U.S. Pat. 4,524,233 (June 18, 1985), W. L. Hsu and co-workers (to The Goodyear Tire and Rubber Co.).
120. V. D. Gostinskii, *Gigiena Truda i Prof. Zabolevaniya* **9**(1), 36 (1965).
121. V. I. D'yachkov, V. K. Mishin, L. N. Berezina, and P. A. Podurueva, *Sb. Nauch. Tr. Kuibyschev. Nauch. Issled. Inst. Gig.* (7), 94 (1972).
122. S. A. Pigolev, *Sb. Nauch. Tr. Kuibyschev. Nauch. Issled. Inst. Gig.* (6), 64 (1971).
123. A. S. Fauston, *Tr. Voronezh. Med. Ist.* (87), 10 (1972).
124. *Isoprene Technical Data*, Bulletin No. 1, Goodrich-Gulf Chemicals, Inc., Cleveland, Ohio, 1968.
125. D. G. Hendry, Stanford Research Institute, Menlo Park, Calif., private communication, 1972.
126. *Chem. Eng. News* **34**, 292 (1956).

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