Kirk-Othmer Encyclopedia of Chemical Technology.

POLYISOPRENE

The preparation of a synthetic polyisoprene was first reported in 1879 by Bouchardat (1), who treated isoprene [78-79-5] obtained from the destructive distillation of natural rubber with hydrochloric acid. This discovery led to a search for a way of converting isoprene into a material duplicating natural rubber (*Hevea brasilienses*). During World War II, scientists extensively studied the polymerization of isoprene with the hope of replicating natural rubber since the United States was temporarily cut off from sufficient natural rubber supplies. These studies were not successful. Finally, in 1954 the B.F. Goodrich Co. was successful in preparing a synthetic *cis*-1,4-polyisoprene [9003-31-0] through use of the newly discovered Ziegler transition-metal halide coordination-type catalyst (2, 3). This catalyst consisted of a trialkylaluminum and titanium tetrachloride. Soon afterward, the Firestone Tire and Rubber Co. revealed a synthesis of *cis*-1,4-polyisoprene with a catalyst based on lithium metal (4). This catalyst yielded a polyisoprene with about 92% *cis*-1,4-structure. After achieving the goal of a synthetic *cis*-1,4-polyisoprene duplicating the structure and properties of natural rubber, workers focused on development of economical processes for commercial manufacture of isoprene monomer and for its commercial polymerization. In 1959–1960 the Shell Oil Co. came on stream with the first commercial plant for producing synthetic *cis*-1,4-polyisoprene using a lithium catalyst. Shortly thereafter, The Goodyear Tire & Rubber Co. began commercial production of *cis*-1,4-polyisoprene using a Ziegler catalyst. Later, in 1967, the B. F. Goodrich Co. began commercial production of synthetic polyisoprene using a Ziegler catalyst.

1. Physical Properties

In Table 1 some of the properties of raw synthetic *cis*-1,4-polyisoprene (Goodyear's Natsyn) and natural rubber (Hevea) are presented along with references that contain additional thermal, optical, electrical, and mechanical property data. Some properties of synthetic *trans*-1,4-polyisoprene (Kuraray TP-301) are also given. Molecular weights and mol wt distribution are determined by gel-permeation chromatography (gpc) (11).

2. Chemical Properties

2.1. Polymer Structure

Isoprene can undergo 1,4-, 1,2-, or 3,4-addition polymerization depending on the catalyst type and conditions, resulting in several structures:

Table 1. Properties of Polyisoprenes

	cis-1,4-Polyisoprene[a]		*trans*-1,4-Polyisoprene[b]	
Property	Natural rubber (Hevea)	Natsyn 2200[c]	Kuraray TP-301[d]	Natural balata
density, g/mL	0.913	0.91	0.96	
refractive index, n_D	1.5191			
Mooney viscosity, ML 1 + 4, 100°C		70–90	30	25–33
ash content, % max	0.5–1.5	0.60	0.15	0.5
T_g, °C	−72	−72		
T_m, °C			67	67
$M_w \times 10^{-5}$		7.55–9.55		
$M_n \times 10^{-5}$		2.4–3.5		
microstructure, nmr				
cis-1,4, mol %	~100%	98.3[e]		
trans-1,4, mol %		1.4	99	~100
3,4, mol %		0.3	0.2	0.2

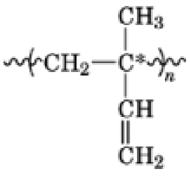
[a] Ref. (5–8).

[b] Ref. 9.

[c] The Goodyear Tire & Rubber Co., Ziegler Ti–Al catalyst.

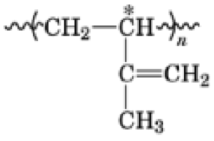
[d] Gel content = 0%; volatile matter = 0.3%.

[e] Cariflex, from Shell Nederland Chemie, and an alkyllithium catalyst (10), has 90.9% *cis*-1,4, 5.2% *trans*-1,4, and 3.9% 3,4.



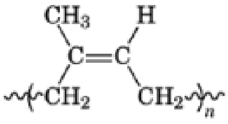
$$\sim\!\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH=CH_2}{C^*}}\right)_n\!\!\sim$$

1,2-polyisoprene

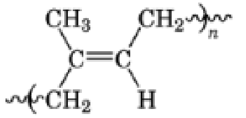


$$\sim\!\!\left(CH_2-\overset{*}{C}H\underset{\displaystyle \overset{|}{C}(=CH_2)CH_3}{}\right)_n\!\!\sim$$

3,4-polyisoprene

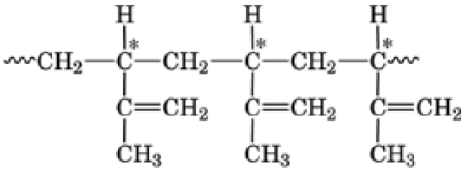


cis-1,4-polyisoprene

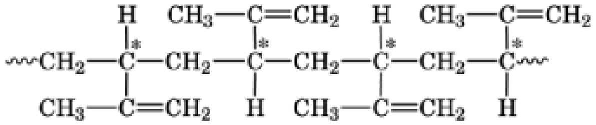


trans-1,4-polyisoprene

For the 1,2- and 3,4-addition, a chiral carbon (marked by an asterisk) is formed which has an *R* or *S* configuration, but there is no net optical activity, because equal amounts of the *R* and *S* configurations are formed. The *R* and *S* configurations along the polymer chains lead to diastereomeric isomers called isotactic, syndiotactic, and atactic. In isotactic polyisoprene all monomer units have the same configuration as illustrated for isotactic 3,4-polyisoprene. In syndiotactic polyisoprene, the monomer units alternate between *R* and *S* configurations as illustrated for syndiotactic 3,4-polyisoprene.



isotactic 3,4-polyisoprene



syndiotactic 3,4-polyisoprene

In atactic polyisoprene, *R* and *S* configurations occur at random. The different modes of enchainment of isoprene (1,2-, 3,4-, *cis*-1,4-, and *trans*-1,4-) and the different stereochemical configurations that are possible result in eight possible stereoregular polyisoprenes. The best known polyisoprenes of high stereoregularity are *cis*-1,4-polyisoprene and *trans*-1,4-polyisoprene. Natural rubber (Hevea, Guayule, tree rubber) and synthetic *cis*-1,4-polyisoprene (Natsyn), currently produced in the United States by The Goodyear Tire & Rubber Co., are examples of *cis*-1,4-polyisoprene. Natural balata and gutta-percha and synthetic *trans*-1,4-polyisoprene, currently produced by the Kuraray Co., Ltd. of Japan, are examples of *trans*-1,4-polyisoprene. A 3,4-polyisoprene of 99–100% 3,4 units (12) has been synthesized. The *cis*-1,4-polyisoprene is a soft rubbery material, whereas the *trans*-1,4-polyisoprene is a hard, crystalline material.

The microstructures of several synthetic *cis*-1,4-polyisoprenes and natural rubber as determined by ^{13}C-nmr (8, 13) are shown in Table 1. ^{1}H-nmr measurements may also be used for microstructure characterization (8, 13–15).

3. Polymerization

3.1. Ziegler-Natta

In 1954, the B. F. Goodrich Co. used the newly discovered Ziegler catalyst for polymerizing ethylene to polyethylene as a catalyst for making *cis*-1,4-polyisoprene (2, 3). The catalyst consisted of titanium tetrachloride and a trialkylaluminum. Aliphatic or aromatic hydrocarbons were used as the polymerization solvents with the exclusion of oxygen and moisture. The method of preparing the Ziegler catalyst and polymerization variables, such as temperature and catalyst level, has been extensively studied (16, 17). The active titanium species is the finely divided brown solid precipitate of $\beta{-}TiCl_3$ (16, 18). The α-, δ-, and γ-crystalline forms of titanium trichloride do not give the *cis*-1,4-microstructure (19) but rather the trans polymer. In a hydrocarbon solvent the two catalyst components, triisobutylaluminum and titanium tetrachloride, react in the absence of monomer to yield a preformed catalyst which was found to be more reactive and gave more reproducible polymerizations than catalysts prepared *in situ* (20). A molar ratio of Al:Ti in the range of 0.9–1.0 appeared optimum for *cis*-1,4-polyisoprene yield (20). Other factors such as catalyst preparation temperature, influence of the R group in the alkylaluminum compound (R_3Al), and catalyst aging have been extensively studied (16, 17). Another variable studied was the effect of electron donors such as ethers and amines on the catalyst (21–24). The optimum molar ratio of ether to titanium was found to be in the range of 0.7 to 0.9, depending on the ether used (16, 25). Modification of the catalyst with aromatic ethers resulted in high activity, a low isoprene oligomer content, and a low polymer gel content (25, 26). The polymerization temperature and catalyst concentration directly influenced the polymer molecular weight and polymerization rate, but apparently did not affect the polymer microstructure. A reduction in the polymerization temperature from 50 to 0°C gave an approximate doubling of the polymer molecular weight as measured by dilute solution viscosity (dsv) (16). The monomer conversion to polymer was directly dependent on the catalyst level (27). However, the polymer molecular weight as measured by dsv was only approximately doubled by a twentyfold decrease in catalyst (26, 28).

High (95–97%) *cis*-1,4-polyisoprene has been prepared with a catalyst consisting of an aluminum hydride derivative (alane) and titanium tetrachloride by the SNAM-Laboratoni Riuniti Studi e Ricerche S. Donato Milanese in Milan, Italy. This catalyst does not contain a direct metal–carbon bond (29). With titanium tetrachloride and $AlHCl_2{\cdot}O(C_2H_5)_2$, a halogen–alane complexed with diethyl ether, in benzene at 5°C, and an Al:Ti molar ratio of 1.6, a 96.5% *cis*-1,4-polyisoprene (by ir analysis) was obtained (29). Other alane-type catalysts contain trialkylamines, NR_3, as the Lewis bases: $AlHCl_2{\cdot}NR_3$, $AlH_2Cl{\cdot}NR_3$, $AlH_3{\cdot}NR_3$ (30). Also, poly(*N*-alkyliminoalanes), $(AlHNR)_n$, in which R is alkyl or phenyl and $n = 4 - 10$, have been utilized with titanium tetrachloride (30). Cyclic polyiminoalanes (PIA), $(AlHNR)_n$, and titanium tetrachloride appeared to give the best performance in terms of activity and polymer molecular weight (31). The polyiminoalanes have been characterized as cyclic oligomers containing 4–10 iminic units.

Another catalyst system for preparing high *cis*-1,4-polyisoprene is based on rare-earth compounds in the lanthanide series, especially neodymium compounds. Chinese workers (32) reported the preparation of a polyisoprene containing 95% *cis*-1,4 units with $Ln(naph)_3{-}(i{-}C_4H_9)_3Al{-}(C_2H_5)_3Al_2Cl_3$ catalyst, where Ln is a rare-earth metal ion and naph is naphthenate. The highest activity catalyst was obtained with neodymium naphthenate which yielded polyisoprene in 96% conversion with 95% *cis*-1,4 and 5% 3,4 microstructure. Preparation of >94% *cis*-1,4-polyisoprene with lanthanide–trialkylaluminum catalysts such as $Nd(naph)_nCl_{3-n}$, where $n = 1$ or 2; $NdCl_3{\cdot}3ROH$; and neodymium trichloride phosphonate was also reported (33). The postulated active species of these catalysts was a bimetallic complex containing an alkylated rare-earth compound:

Polyisoprenes of 94–98% *cis*-1,4 content were obtained with lanthanum, cerium, praseodymium, neodymium, and other rare-earth metal ions (eg, $LnCl_3$) with trialkylaluminum (R_3Al) (34). Also, a $NdCl_3{\cdot}2THF(C_2H_5)_3Al$ catalyst has been used to prepare 95% *cis*-1,4-polyisoprene (35). *cis*-1,4-Polyisoprene of 98% *cis*-1,4 and 2% 3,4 content was obtained with organoaluminum–lanthanide catalysts, $NdCl_3{\cdot}nL$, where L is an electron-donor ligand such as ethyl alcohol or butyl alcohol, or a long-chain alcohol, and n is 1 to 4 (36).

Amorphous (most likely atactic) 3,4-polyisoprene of 94–100% 3,4-microstructure was prepared with a $(C_2H_5)_3Al–Ti(O–n\text{-}C_3H_7)_4$ catalyst (11). Crystalline 3,4-polyisoprene containing about 70% 3,4-units and about 30% *cis*-1,4-microstructure was prepared using a catalyst derived from iron acetyl acetonate, trialkylaluminum, and an amine in benzene (37). However, this polyisoprene contained gel and was obtained in poor yield. Essentially gel-free crystallizable 3,4-polyisoprene of 70–85% 3,4-microstructure with the remainder being cis-1,4 microstructure was prepared in conversions of greater than 95% with a water-modified trialkylaluminum, ferric acetyl acetonate, and 1,10-phenanthroline catalyst (38). The 3,4-polyisoprene is stereoregular and believed to be syndiotactic or isotactic.

In 1955, *trans*-1,4-polyisoprene having a structure identical to that of natural gutta-percha was prepared using a triethylaluminum-α-titanium trichloride catalyst (39). Since then, vanadium catalysts, especially vanadium trichloride, with trialkylaluminums have been found to be the most active and stereospecific, and give the highest yields of *trans*-1,4-polyisoprene (17). Polymerization of isoprene in heptane using trialkylaluminium–vanadium trichloride catalyst yielded very high *trans*-1,4-polyisoprene (40), and a triethylaluminum–vanadium trichloride catalyst gave about 97% *trans*-1,4 microstructure (nmr analysis) (41). Modification of the trialkylaluminum–vanadium trichloride catalyst with ethers, such as diisopropyl ether, increased the polymer yield (42). Increased polymer yields have also been obtained with vanadium trichloride deposited on inert supports, eg, kaolin (43).

3.2. Alfin Catalysts

Alfin catalysts (44, 45) give polyisoprenes of high *trans*-1,4 microstructure (46). For example, a typical Alfin catalyst gives polyisoprene of 52% *trans*-1,4, 27% *cis*-1,4, 16% 3,4, and 5% 1,2 content (ir analysis) (46). One type of Alfin catalyst consists of allylsodium, sodium isopropoxide, and sodium chloride (47, 48). Because of the mixed microstructure polyisoprene produced, Alfin catalysts are not used commercially.

3.3. Alkali Metal Catalysts

The polymerization of isoprene with sodium metal was reported in 1911 (49, 50). In hydrocarbon solvent or bulk, the polymerization of isoprene with alkali metals occurs heterogeneously, whereas in highly polar solvents the polymerization is homogeneous (51–53). Of the alkali metals, only lithium in bulk or hydrocarbon solvent gives over 90% *cis*-1,4 microstructure. Sodium or potassium metals in n-heptane give no *cis*-1,4 microstructure, and 48–58 mol % *trans*-1,4, 35–42% 3,4, and 7–10% 1,2 microstructure (46). Alkali metals in benzene or tetrahydrofuran with crown ethers form solutions that readily polymerize isoprene; however, the 1,4 content of the polyisoprene is low (54). For example, the polyisoprene formed with sodium metal and dicyclohexyl-18-crown-6 (crown ether) in benzene at 10°C contains 32% 1,4-, 44% 3,4-, and 24% 1,2-isoprene units (54).

High *cis*-1,4-polyisoprene was prepared using finely divided lithium metal in petroleum jelly as catalyst in 1956 (55). The bulk polymerization started after an induction period, and the polymerization mass thickened and became solid. Polyisoprene of low gel, high inherent viscosity, and up to 94% *cis*-1,4 content (the remainder was 3,4) was obtained. A lithium metal dispersion in hexane or heptane also gave high *cis*-1,4-polyisoprene (46, 56), whereas lithium metal dispersions in polar solvents such as tetrahydrofuran (THF), diethyl ether, and dioxane gave essentially no *cis*-1,4 microstructure (46). For example, in THF polyisoprene of 34 mol % *trans*-1,4-, 52% 3,4-, and 14% 1,2- was produced (46). In the late 1950s, the lithium dispersions were generally replaced by organolithium compounds, which were easier to handle, gave homogeneous systems, and could be used without obtaining the poorly reproducible induction times that attended use of lithium metal.

Table 2. Effect of Polymerization Solvent on Polyisoprene Microstructure

			Mol %[a]		
Initiator	Solvent	Temperature, °C	*cis*-1,4	*trans*-1,4	3,4
n-C_4H_9Li	cyclohexane	30	80	15	5
sec-C_4H_9Li	benzene	20	71	23	6
sec-C_4H_9Li	THF	30	0	69	31

[a] Precision of 300 MHz ^{1}H nmr: *cis*-1,4 or $trans-1,4=\pm2\%$; 3,4 or $1,2=\pm1\%$. 1,2 measured 0% in all three cases.

3.4. Anionic Polymerization

Polyisoprenes of predictable molecular weight and uniform chain length can be prepared by anionic polymerization, which is characterized by living growing chains and the absence of chain-termination (57–61). Therefore, polyisoprenes of predictable molecular weight can be prepared from simple stoichiometry. Very narrow molecular weight distributions, approaching the Poisson distribution, are possible. Organolithiums, especially the butyllithiums, are most frequently utilized as initiators of the anionic polymerization of isoprene since they are soluble in both polar and nonpolar solvents. Both *sec*- and *tert*-butyllithiums have higher initiation rates than that of n-butyllithium (16). The polymerization solvent profoundly influences the polyisoprene microstructure as shown in Table 2 (62, 63).

A change from an aliphatic or aromatic hydrocarbon solvent (cyclohexane, benzene) to a polar solvent (THF) leads to a large increase in *trans*-1,4 and 3,4 microstructure (58). Organolithium compounds are highly associated; *sec*-butyllithium in benzene or cyclohexane exists as a tetramer, and n-butyllithium as a hexamer (64, 65). This association in hydrocarbon solvents results partly in the slow initiation observed between some organolithiums and isoprene (66). At low initiator concentrations, the polymerization rate of isoprene in alkyllithium polymerization is proportional to monomer and alkyllithium concentrations (67). 3,4-Polyisoprenes are obtained by modification of the lithium polymerization with ethers, such as the dialkyl ethers of ethylene glycol or tertiary amines (68, 69).

3.5. Cationic Polymerization

A small amount of isoprene is cationically copolymerized with isobutylene in the commercial process for making butyl rubber, wherein the isoprene provides the unsaturation required for sulfur vulcanization. Homopolymerization of isoprene by cationic catalysts can lead to cyclized products and loss of unsaturation (70, 71), as for example, during polymerizations initiated by boron trifluoride (72). Cationic polymerization of isoprene with BF_3, $SnCl_4$, or $AlCl_3$ catalysts in pentane, chloroform, or ethylbenzene from -78 to 30°C at around 50% conversion gives about 90% *trans*-1,4-polyisoprene structure; the balance is 1,2 and 3,4 microstructure (no *cis*-1,4 microstructure) (73). An insoluble powder was formed by cyclopolymerization of isoprene using titanium tetrachloride/Grignard reagent (74) or ethylaluminum dichloride (75).

3.6. Free-Radical Polymerization

The best method for polymerizing isoprene by a free-radical process is emulsion polymerization. Using potassium persulfate [7727-21-1] as initiator at 50°C, a 75% conversion to polyisoprene in 15 h was obtained (76). A typical emulsion polymerization recipe is given as follows (77).

Ingredient	Parts by wt
water	180
isoprene	100
potassium fatty acid soap	5
potassium chloride	1
potassium persulfate	0.15–0.60
tert-dodecyl mercaptan	0.1–0.8

The predominant microstructure obtained by emulsion polymerization is *trans*-1,4, determined by ir, as shown in mol % for two temperatures and initiators (72).

Initiator	*cis*-1,4	*trans*-1,4	3,4	1,2
cumene hydroperoxide at 5°C	1.7	86.2	5.4	6.7
potassium persulfate at 50°C	17.6	71.9	5.3	5.2

Since emulsion polyisoprene has low *cis*-1,4 microstructure, it has poorer physical properties than the high *cis*-1,4-polyisoprene and has not been commercialized.

4. Manufacture and Processing

Currently, *cis*-1,4-polyisoprene is manufactured in the United States only by The Goodyear Tire & Rubber Co. at Beaumont, Texas. In Western Europe, only the Shell Nederland Chemie (Royal Dutch/Shell Group) commercially produces *cis*-1,4-polyisoprene; in Japan, the producers are Japan Synthetic Rubber Co., Ltd. and Nippon Zeon Co., Ltd. The sole world producer of *trans*-1,4-polyisoprene is Kuraray Co., Ltd. in Japan.

Dry prepurified isoprene monomer and dry aliphatic hydrocarbon solvent along with a Ziegler catalyst consisting of triisobutylaluminum and titanium tetrachloride are utilized in one commercial solution process for *cis*-1,4-polyisoprene. Isoprene, the Ziegler catalyst, and recycled aliphatic hydrocarbon solvent in an inert atmosphere (nitrogen) are continuously fed into a continuous polymerization reactor system, and the isoprene is polymerized to the desired conversion. As the polymerization stream leaves the reactor system, a shortstop and an antioxidant are added to stop the polymerization and protect the polyisoprene throughout the finishing operation. The shortstopped polymerization stream then proceeds to the steam stripping operation, where the unreacted isoprene monomer and aliphatic hydrocarbon solvent are removed. After separation and purification, the isoprene and aliphatic hydrocarbon solvent are recycled back to the beginning of the process. The rubber crumb from the stripping operation is fed through dewaterers and dryers to obtain dry rubber crumb. The dried rubber crumb is baled and packaged in 50 μm (2.0 mil) polyethylene film. The bales weigh about 34 kg. Modern polymerization plants such as Goodyear's at Beaumont, Texas employ the latest process design and computer controls for efficient operation. An on-site cogeneration power plant allows efficient use of high pressure steam to run equipment and provide a large portion of the plant's electrical needs. Air emissions and wastewater are treated to meet environmental laws and regulations. Over 95% of the liquid wastes generated by the plant are reused (78). Detailed flow sheets of commercial plants have been published (79, 80). The microstructures of two commercial *cis*-1,4-polyisoprenes (Natsyn and Cariflex) prepared with two different catalysts and natural rubber are compared in Table 1.

4.1. Compounding

Another important part of the use of polyisoprene rubber is its compounding into formulations that can be utilized to make finished goods and articles. The raw polyisoprene rubber is mixed in a Banbury (internal) mixer or on a mill with ingredients such as fillers (carbon black, clays, or silicates), plasticizers, antioxidants, accelerators, and sulfur. The filler, eg, carbon black, gives durability and reduces cost of the compound. The sulfur functions as a cross-linking agent for the highly unsaturated polyisoprene. The accelerators, eg, sulfenamides, thiazoles, guanidines, thiuram sulfides, and thiocarbamates, help reduce the vulcanization time. The antioxidants (qv), eg, arylamines, hindered phenols, etc, retard the deterioration of the finished article due to aging. Antiozonants (qv), eg, *p*-phenylenediamine, and waxes are also used in tire formulations to retard cracking under stress. The resulting rubber compound is calendered, molded, extruded, or fabricated into the desired shape and vulcanized or cured at around 150°C.

In Tables 3 and 4 typical formulations and properties are shown for black-filled stocks of natural rubber and synthetic *cis*-1,4-polyisoprene and a blend of the two. Although black-filled stocks of synthetic polyisoprene and natural rubber exhibit many similar properties, the tackiness and green strength of synthetic polyisoprene are inferior. However, synthetic polyisoprene exhibits a uniform cure rate that can lead to automation in production of rubber parts. Blends of synthetic polyisoprene and natural rubber can smooth out processing or cure variations of pure natural rubber. Synthetic polyisoprene is also blended with other general-purpose elastomers such as *cis*-1,4-polybutadiene and styrene–butadiene rubber (SBR) to obtain combinations of properties not available with a single elastomer. For example, the tear and tensile strengths of a polyisoprene compound can be increased by blending with *cis*-polybutadiene and SBR. Compounding information and formulations are available from polymer and rubber chemical producers (5, 6, 81).

Table 3. Black-Loaded Formulation for Natsyn and Natural Rubber[a]

Ingredient	Compound 1, phr	Compound 2, phr	Compound 3, phr
Natsyn 2200	100.00		50.00
natural rubber SMR-L		100.00	50.00
zinc oxide	3.00	3.00	3.00
stearic acid	2.00	1.00	1.50
Wingstay 100[b]	1.25	0.25	0.75
N-330 carbon black	40.00	40.00	40.00
naphthenic oil	5.00	5.00	5.00
Santocure[c]	1.20	1.20	1.20
Unads[d]	0.20	0.10	0.15
sulfur	2.00	2.00	2.00
Total	*154.65*	*152.55*	*153.60*

[a] Ref. 5. Best cure, 150°C for 20 min; phr by weight.
[b] Mixed diaryl–*p*-phenylenediamines, antioxidant of The Goodyear Tire & Rubber Co.
[c] Accelerator of Monsanto Co.
[d] Tetramethylthiuram monosulfide, accelerator of R. T. Vanderbilt Co.

5. Economic Aspects

In 1993, synthetic *cis*-1,4-polyisoprene was manufactured commercially in the United States only by The Goodyear Tire and Rubber Co. at Beaumont, Texas. This plant has a capacity of 61,000 metric tons/yr and utilizes a Ziegler catalyst (83). Since 1985, annual production of polyisoprene has been flat at about 48,000 to 49,000 metric tons (84). In 1990, Bayer AG purchased Polysar, Inc. and the former B. F. Goodrich Co. polyisoprene plant at Orange, Texas which is on inactive status and has an estimated potential annual capacity

Table 4. Properties of Black-Filled Stocks for Natsyn and Natural Rubber[a]

Property	Compound 1	Compound 2	Compound 3
tensile strength, MPa[b,c]	23.1	25.9	26.2
elongation, %	460	480	490
300% modulus, MPa[c]	12.6	12.4	12.8
Shore A hardness	68	65	66
tear strength, kN/m[d]	58.1	72.3	60.6
compression set, 22 h at 70°C, %	10.9	16.6	10.9
Goodyear-Healey rebound pendulum test[e]			
cold rebound, %	74.6	79.8	78.6
hot rebound, %	85.9	87.7	87.1
MST abrasion resistance	119	168	165
green strength			
stress at yield, MPa[c]	0.28	0.38	0.33
ultimate tensile, MPa[c]	0.43	2.35	1.41
ultimate elongation, %	1950	630	760

[a] Ref. 5. Formulation of Table 3.
[b] Scott tensile, die C, 50 cm/min.
[c] To convert MPa to psi, multiply by 145.
[d] To convert kN/m to ppi, multiply by 5.71.
[e] ASTM D1054, Ref. 82.

of 55,000 metric tons. The only Western European producer of synthetic *cis*-1,4-polyisoprene is Shell Nederland Chemie (member of the Royal Dutch/Shell Group) with a plant at Pernis, (near Rotterdam) Netherlands with an annual estimated plant capacity of 75,000 metric tons in 1983 (84, 85). The plant capacity has since been reduced to about 45,000 metric tons per year (83). In 1989, the estimated production of *cis*-1,4-polyisoprene in Western Europe was 20,000 metric tons (84). In 1989 in Japan, the annual production capacity for synthetic *cis*-1,4-polyisoprene was about 72,000 metric tons with Japan Synthetic Rubber Co., Ltd. having an annual capacity of 35,000 metric tons, and Nippon Zeon Co., Ltd. having an annual capacity of 37,000 metric tons. In 1989, the estimated production of *cis*-polyisoprene in Japan was 55,000 metric tons (84). In 1992, Coperbo in Brazil, South America was to start up a plant with an estimated annual capacity of 35,000 metric tons/yr (83, 84). In 1990, in the USSR and other European Centrally Planned Economy Countries, the total plant capacity for synthetic polyisoprene was estimated to be about six times as large as the rest of the world. In the USSR, the production capacity was about 960,000 metric tons/yr, and in 1989, an estimated 770,000 metric tons were produced (84). In mid-1992, the former Soviet Union (Commonwealth of Independent States) was expected to reduce its output and capacity for synthetic polyisoprene to about 75% of its current level (86).

trans-1,4-Polyisoprene is not produced commercially in the United States, although the 1990 consumption was estimated to be around 2000 metric tons (synthetic and natural) (84). The *trans*-polyisoprene is used mainly for golf ball covers for premium golf balls and for medical applications. In Japan, Kuraray Co., Ltd. produces about 400 metric tons/yr of *trans*-1,4-polyisoprene (84).

In 1989, the estimated United States consumption of synthetic polyisoprene was 51,000 metric tons, and of natural rubber 890,000 metric tons (84). The price for synthetic *cis*-1,4-polyisoprene, namely, Natsyn 2200, Natsyn 2205, or Natsyn 2210 in the United States in August, 1992, was $1.98/kg in carload or truckload quantities fob at Beaumont, Texas (87). The price of synthetic *trans*-1,4-polyisoprene from Kuraray Co., Ltd. in the United States was $21.80/kg in 545-kg lots (88).

6. Specifications, Standards, Quality Control

Specifications for solid *cis*-1,4-polyisoprenes are shown in Table 5 and include analyses for volatile matter, extractables, ash, and Mooney viscosity at 100°C. Standard method ASTM D1416 includes chemical analysis methods for volatile matter, extractables, and total ash, while ASTM D1646 includes Mooney viscosity (82). The Monsanto rheometer data for vulcanizates prepared by a standard recipe may also be specified. This formulation for vulcanizate (ASTM D3403) is mixed in a Banbury mixer in two passes with all but sulfur and accelerator added in first pass:

Material	Phr
Natsyn polyisoprene	100.0
HAF black	35.00
stearic acid	2.00
zinc ozide	5.00
Santocure NS	0.70
sulfur	2.25
Total	*144.95*

Table 5. Specifications of *cis*-1,4-Polyisoprenes[a]

Property	Natsyn 2200	Natsyn 2205[b]	Natsyn 2210	ASTM test method
raw polymer				
volatile matter, % max	0.5	0.5	0.5	D1416
extractables, % max	3.0	3.0	3.0	D1416
ash, % max	0.6	0.6	0.6	D1416
Mooney, ML-4 at 100°C	70–90	70–90	50–65	D1646
vulcanizate[c] torque [d]N·m[e]				
minimum	0.61–0.90	0.61–0.90	0.51–0.85	
maximum	3.78–4.30	3.78–4.30	3.38–4.17	
t', min[f]	5.8–8.2	5.8–8.2	5.8–8.8	
$t'50$, min	8.7–12.3	8.7–12.3	8.2–12.7	
$t'90$, min[g]	12.8–16.8	12.8–16.8	12.4–16.9	

[a] Goodyear Chemicals Product Specification Sheets: Natsyn 2200 (Sept. 17, 1991); Natsyn 2205 (Sept. 17, 1991); Natsyn 2210 (May 9, 1990).

[b] Gel particles $_{>1.0\ \mathrm{mm}}$, none; 0.5 to 1.0 mm, 4 max.

[c] Formulation for vulcanizate ASTM D3403.

[d] Monsanto rheometer at 150°C, 1 deg arc, 1.7 Hz, 30 min chart, ASTM D2084.

[e] To convert N·m to in.-lb., multiply by 8.85.

[f] Rise above minimum torque with 1 arc.

[g] Time to maximum torque.

7. Health and Safety Factors

Polyisoprene rubber is relatively nonhazardous, but must be kept away from sparks, open flames, or excessive heat because it will burn. The current Material Safety Data Sheet (MSDS) should always be checked for known hazards before using polyisoprene or any other chemical materials.

8. Uses

cis-1,4-Polyisoprene is used in tires and tire products, belts, gaskets, hoses, foam rubber, molded and mechanical goods, bottle nipples, gloves, caulking, sealants, footwear and sporting goods, rubber bands, erasers, and rubber sheeting. Synthetic *cis*-1,4-polyisoprene and natural rubber have the same type of applications because of their similar structure and properties. About 60% of the synthetic *cis*-1,4-polyisoprene was used in tires and tire products in 1989 (84, 89), and about 12% in mechanical goods. Footwear, especially sports footwear, accounted for about 4% of the polyisoprene consumption in 1989; all other applications accounted for 24%. Both synthetic *cis*-1,4-polyisoprene and natural rubber are used in construction of radial passenger car tire carcasses because of their good green strength and building tack. However, polyisoprene is not normally used in passenger car tire treads. Generally, passenger car tire treads consist of blends of polybutadiene and styrene–butadiene rubber (SBR) (84, 89). The mechanical goods application area includes molded automotive goods, dairy industry products, and medical applications. Also, synthetic *cis*-1,4-polyisoprene is used in heavy-duty truck and bus tire treads where outstanding treadwear and low heat buildup under heavy loads are important.

Since *trans*-1,4-polyisoprene is a crystalline thermoplastic, it resists abrasion, scuffing, and cutting, and is used mainly in high quality golf ball covers and orthopedic devicesand splints, and to some extent in transmission belts, cable coverings, and adhesives (84). *trans*-1,4-Polyisoprene is used in prosthetics, splints, braces, casts, and attachments for artificial limbs because it possesses an unusual combination of properties (90). *trans*-Polyisoprene is a tough, rigid, durable, and lightweight material at room temperature, but when immersed in hot water, it softens and does not crystallize immediately as it cools to body temperature, thereby permitting molding directly to a patient's body.

3,4-Polyisoprene is finding some applications in specialty tire rubber compounds (69, 91).

BIBLIOGRAPHY

"Elastomers, Synthetic (Polyisoprene)" in *ECT* 3rd ed., Vol. 8, pp. 582–592, by H. Tucker and S. E. Horne, Jr., B.F. Goodrich Co.

Cited Publications

1. G. Bouchardat, *Compt. Rend.* **89**, 1117 (1879).
2. Belg. Pat. 543,292 (June 2, 1956), (to Goodrich-Gulf Chemical Co.).
3. S. E. Horne and co-workers, *Ind. Eng. Chem.* **48**, 784 (1956).
4. F. W. Stavely and co-workers, *Ind. Eng. Chem.* **48**, 778 (1956).
5. *Natsyn Polyisoprene Rubber Bulletin*, Goodyear Chemical Division, The Goodyear Tire & Rubber Co., Akron, Ohio, Oct., 1988.
6. K. A. Valin in R. F. Ohm, ed., *The Vanderbilt Rubber Handbook*, R. T. Vanderbilt Co., Inc., Norwalk, Conn., 1990, p. 44.
7. L. A. Wood in J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., John Wiley & Sons, Inc., New York, 1989, pp. V/7 and V/8.
8. D. R. Burfield and Y. Tanaka, *Polymer* **28**, 907 (1987).
9. *Kuraray TP Technical Information No. 731, Kuraray Trans Polyisoprene TP-301*, Kuraray Isoprene Chemical Co., Ltd., Synthetic Rubber Dept., 3-8-2, Nihonbashi, Chuo-Ku, Tokyo, Japan, Oct. 1, 1982.
10. A. F. Halasa, *Rubber Chem. Technol.* **55**, 253 (1982).
11. J. Cazes, *J. Chem. Ed.* **43**, A567 (1966).
12. G. Natta, L. Porri, and A. Carbonaro, *Makromol. Chem.* **77**, 126 (1964).
13. Y. Tanaka, *Rubber Chem. Technol.* **64**, 325 (1991).
14. H. Sato, A. Ono, and Y. Tanaka, *Polymer* **18**, 580 (1977).
15. H. Sato and Y. Tanaka, *J. Polym. Sci., Polym. Chem. Ed.* **17**, 3551 (1979).

16. E. Schoenberg and co-workers, *Rubber Chem. Technol.* **52**, 526 (1979).
17. L. Porri and A. Giarrusso in G. Allen and J. C. Bevington, eds., *Comprehensive Polymer Science*, Vol. **4**, Pergamon Press, Inc., Elmsford, N.Y., 1989, 53–108.
18. G. Natta and co-workers, *Rend. Acad. Naz. Lincei* **24**(8), 121 (1958).
19. G. Natta, L. Porri, and L. Fiore, *Gazz. Chim. It.* **89**, 761 (1959).
20. E. Schoenberg, D. L. Chalfant, and R. H. Mayor, *Rubber Chem. Technol.* **37**, 103 (1964).
21. T. L. Brown, *Adv. Organomet. Chem.* **3**, 365 (1965).
22. U.S. Pat. 3,165,503 (Jan. 12, 1965), (to Goodrich-Gulf, Inc.).
23. Ger. Pat. 1,301,487 (Nov. 20, 1969), (to Chemische Werke Huls, AG).
24. Belg. Pat. 726,446 (June 16, 1969), (to Farbenfab, Bayer AG).
25. E. Schoenberg and co-workers, *Metal Alkyl Catalyzed Polymerizations*, ACS Symposium Series, Div. Ind. Eng. Chem, New York, Sept., 1963.
26. W. M. Saltman, F. S. Farson, and E. Schoenberg, *Rubber and Plastics Age (London)* **46**, 502 (1965).
27. C. F. Gibbs and co-workers, *Rubber World* **144**(1), 69 (1961).
28. S. Y. Bresler and co-workers, *Rubber Chem. Technol.* **33**, 689 (1960).
29. W. Marconi and co-workers, *Makromol. Chem.* **71**, 118 and 134 (1964).
30. A. Mazzei, S. Cucinella, and W. Marconi, *Makromol. Chem.* **122**, 168 (1969).
31. A. Balducci and co-workers, *Rubber Chem. Technol.* **48**, 736 (1975).
32. Academia Sinica, *Sci. Sin.* **17**, 656 (1974).
33. J. Ouyang, F. Wang, and Z. Shen, *Proceedings of China-U.S. Bilateral Symposium on Polymer Chemistry and Physics*, Science Press, Van Nostrand Reinhold Co., New York, 1981, p. 382.
34. Z. Shen and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **18**, 3345 (1980).
35. J. H. Yang and co-workers, *Macromolecules* **15**, 230 (1982).
36. H. L. Hseih and H. C. Yeh, *Rubber Chem. Technol.* **58**, 117 (1985).
37. Sun and Wang, *Acta Polymerica Sinica* **2**, 145 (1988).
38. U.S. Pat. 5,082,906 (Jan. 21, 1992), A. F. Halasa and W. L. Hsu (to The Goodyear Tire & Rubber Co.).
39. Ital. Pat. 536,631 (Dec. 7, 1955), G. Natta, L. Porri, and G. Mazzanti (to Montecatini SpA).
40. G. Natta and co-workers, *Chim. Ind. Milan* **40**, 362 (1958) J. Boor, Jr., *Ziegler-Natta Catalysts and Polymerizations*, Academic Press, Inc., New York, 1979, pp. 145, 146, and 155.
41. E. G. Lovering and W. B. Wright, *J. Polym. Sci., Part A-1* **6**, 2221 (1968).
42. W. Cooper and co-workers, *J. Polym. Sci., Part C* **4**, 211 (1964).
43. J. S. Lasky, H. K. Garner, and R. H. Ewart, *Ind. Eng. Chem. Prod. Res. Dev.* **1**, 82 (1962).
44. A. A. Morton, E. E. Magat, and R. L. Letsinger, *J. Am. Chem. Soc.* **69**, 950 (1947).
45. A. A. Morton, *Ind. Eng. Chem.* **42**, 1488 (1950).
46. A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.* **40**, 73 (1959).
47. V. L. Hansley and H. Greenberg, *Rubber Age* **94**, 87 (1963).
48. A. A. Morton in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. **1**, 1st ed., Wiley-Interscience, New York, 1964, p. 629.
49. Brit. Pat. 24,790 (Oct. 25, 1911), F. E. Matthews and E. H. Strange.
50. C. H. Harries, *Ann. Chem.* 383, 184 (1911).
51. A. Essel and co-workers, *J. Polym. Sci. Polym. Chem. Ed.* **13**, 1847 (1975).
52. A. Essel, R. Salle, and Q. T. Pham, *J. Polym. Sci. Polym. Chem. Ed.* **13**, 1869 (1975).
53. R. Salle and co-workers, *J. Polym. Sci. Polym. Chem. Ed.* **13**, 1855 (1975).
54. S. Alev. F. Schue and B. Kaempf, *J. Polym. Sci. Polym. Lett. Ed.* **13**, 397 (1975).
55. F. W. Stavely and co-workers, *Ind. Eng. Chem.* **48**, 778 (1956) *Rubber Chem. Technol.* **29**, 673 (1956).
56. H. F. Diem, H. Tucker, and C. F. Gibbs, *Rubber Chem. Technol.* **34**, 191 (1961).
57. J. E. McGrath, ed., *Anionic Polymerization, Kinetics, Mechanisms, and Synthesis, ACS Symposium Series No. 166*, American Chemical Society, Washington, D.C., 1981.
58. M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, Inc., New York, 1983.
59. R. N. Young, R. P. Quirk, and L. J. Fetters in R. N. Young, R. P. Quirk, and L. J. Fetters *Advances in Polymer Science*, Vol. **56**, Springer-Verlag, New York, 1984, p. 1.
60. M. Szwarc in M. Szwarc *Advances in Polymer Science*, Vol. **49**, Springer-Verlag, New York, 1983, p. 1.

61. A. Noshay and J. E. McGrath, *Block Copolymers Overview and Critical Survey*, Academic Press, Inc., New York, 1977.
62. D. J. Worsfold and S. Bywater, *Can. J. Chem.* **42**, 2884 (1964).
63. F. Schue, D. J. Worsfold, and S. Bywater, *Macromolecules* **3**, 509 (1970).
64. S. Bywater and D. J. Worsfold, *J. Organomet. Chem.* **10**, 1 (1967).
65. M. Morton and R. A. Pett, and L. J. Fetters, *Macromolecules* **3**, 333 (1970).
66. M. Morton and L. J. Fetters, *Rubber Chem. Technol.* **48**, 359 (1975).
67. H. L. Hsieh, *J. Polym. Sci., Part A* **3**, 153 (1965).
68. K. H. Nordsiek, *Kautsch. Gummi Kunstst.* **35**, 1032 (1982).
69. K. H. Nordsiek and J. Wolpers, *Kautsch. Gummi Kunstst.* **43**(9), 755 (1990) U.S. Pat. 4,894,425 (Jan. 16, 1990) W. Hellermann, K. H. Nordsiek, and J. Wolpers (to Huels Aktiengesellschaft).
70. W. Cooper in P. H. Plesch, ed., *The Chemistry of Cationic Polymerization*, The Macmillan Publishing Co., New York, 1963, p. 349.
71. J. P. Kennedy, *Cationic Polymerization of Olefins: A Critical Inventory*, John Wiley & Sons, Inc., New York, 1975, 164–166.
72. W. S. Richardson and A. Sacher, *J. Polym. Sci.* **10**, 353 (1953).
73. W. S. Richardson, *J. Polym. Sci.* **13**, 325 (1954).
74. N. G. Gaylord and co-workers, *J. Am. Chem. Soc.* 85, 641 (1963).
75. I. Kossler, M. Stolka, and K. Mach, *J. Polym. Sci. Part C* **4**, 977 (1964).
76. C. S. Marvel and J. L. R. Williams, *J. Polym. Sci.* **4**, 265 (1949).
77. M. Morton, J. A. Cala, and I. Piirma, *J. Polym. Sci.* **15**, 167 (1955).
78. *Goodyear-Beaumont Chemical Plant Booklet*, Goodyear Chemical Division, The Goodyear Tire & Rubber Co., Akron, Ohio, 1992.
79. R. L. Magovern and S. L. Soder, *Polyisoprene, Report No. 82, Process Economics Program*, Stanford Research Institute, Menlo Park, Calif., Dec., 1972.
80. *Hydrocarbon Proc.* **50**, 199–200 (Nov., 1971).
81. M. Morton, *Rubber Technology*, 3rd ed., Van Nostrand Reinhold, New York, 1987, 235–259 M. Morton, *Rubber Technology*, 2nd ed., Robert E. Krieger Publishing Co., Malabar, Fl., 1973, 274–301 and 19–113.
82. R. A. Storer, ed., *1990 Annual Books of ASTM Standards*, Vol. **09.01**, ASTM, Philadelphia, Pa., 1990, pp. 227, 307, Section 9.
83. *Rubber Statistical Bulletin*, Vol. **45**, No. 11, The International Rubber Study Group, Wembley, UK, Aug., 1991, p. 47.
84. J. F. Auchter, *Polyisoprene Elastomers, Chemical Economics Handbook*, CEH Product Review, SRI International, Menlo Park, Calif., Jan., 1991.
85. *Rubber Statistical Bulletin*, Vol. **37**, No. 4, The International Rubber Study Group, London, Jan., 1983, p. 49.
86. B. Davis, *Rubber & Plastics News* **21**(27), 6 (July 6, 1992).
87. Technical data, The Goodyear Tire & Rubber Co., Akron, Ohio, Aug. 1, 1992.
88. E. L. Puskas, Co., Akron, Ohio, Sales Agents and Distributors for Kuraray Co., Ltd., (Japan), *Trans*-Polyisoprene TP-301, Dec., 1991.
89. B. F. Greek, *Chem. Eng. News* **69**(19), 37 (May 13, 1991).
90. E. J. Buckler, *Can. J. Chem. Eng.* **62**(1), 3 (1984).
91. H. Takino and co-workers, *Kautsch. Gummi Kunstst.* **43**(9), 761 (1990).

MICHAEL SENYEK
The Goodyear Tire & Rubber Co.

Related Articles

Elastomers, synthetic, introduction; Tire cord; Rubber, natural