Kirk-Othmer Encyclopedia of Chemical Technology.

POLYBUTADIENE

1,3-Butadiene [106-99-0] can be polymerized to produce various resinous and elastomeric polymers. The basic microstructural units in polybutadiene [9003-17-2] include *cis*-1,4, *trans*-1,4, and 1,2 units. A variety of polymers with different properties can be produced by changing the ratio of these units and their tacticity. For example, polybutadienes with high 1,2 contents include syndiotactic polybutadiene with various melting points; isotactic polybutadiene with a melting temperature, T_{m}, of 170°C; and amorphous atactic polybutadiene (T_g = +5°C). High *trans*-1,4-polybutadiene is a resinous crystalline material with three crystal structure modifications having T_{m}s of 55, 150, and 175°C. High *trans*-1,4-polybutadiene [40022-02-4] is partially amorphous when it contains either *cis*-1,4 or 1,2 units which disrupt its crystal structure and reduce its melting point by as much as 20–60°C. It has a glass-transition temperature of $-80°\mathrm{C}$. Other useful elastomers made from 1,3-butadiene include high (99%) *cis*-1,4-polybutadiene [40022-03-5] with a T_{m} of $-13°\mathrm{C}$ and a T_{g} of $-100°\mathrm{C}$, and a mixed microstructure polybutadiene composed of various ratios of *cis*-1,4, *trans*-1,4, and 1,2 units.

The preparation and characterization of 1,3-butadiene monomer is discussed extensively elsewhere (1–4) (see Butadiene). Butadiene monomer can be purified by a variety of techniques. The technique used depends on the source of the butadiene and on the polymerization technique to be employed. Emulsion polymerization, which is used to make amorphous *trans*-1,4-polybutadiene (75% *trans*-1,4; 5% *cis*-1,4; 20% 1,2), is unaffected by impurities during polymerization. However, both anionic and Ziegler polymerizations, which are used to prepare *cis*-1,4-polybutadiene, mixed *cis*-1,4 and *trans*-1,4-polybutadiene, and high 1,2-polybutadiene [26160-98-5], are greatly affected by impurities. During polymerization, oxygenated compounds such as alcohols, aldehydes or ketones and acidic compounds such as organic acids must be avoided.

Between the 1920s when the initial commercial development of rubbery elastomers based on 1,3-dienes began (5–7), and 1955 when transition metal catalysts were first used to prepare synthetic polyisoprene, researchers in the U.S. and Europe developed emulsion polybutadiene and styrene–butadiene copolymers as substitutes for natural rubber. However, the tire properties of these polymers were inferior to natural rubber compounds. In seeking to improve the synthetic material properties, research was conducted in many laboratories worldwide, especially in the U.S. under the Rubber Reserve Program.

The discovery by Ziegler that ethylene and propylene can be polymerized with transition-metal salts reduced with trialkylaluminum gave impetus to investigations of the polymerization of conjugated dienes (7–9). In 1955, synthetic polyisoprene (90–97% *cis*-1,4) was prepared using two new catalysts. A transition-metal catalyst was developed at B. F. Goodrich (10) and an alkali metal catalyst was developed at the Firestone Tire & Rubber Co. (11). Both catalysts were used to prepare *cis*-1,4-polyisoprene on a commercial scale (9–19).

The Firestone group also polymerized 1,3-butadiene to give an extremely high mol wt polybutadiene of 70% *cis*-1,4 structure. In their research, they purposefully avoided the preparation of vinyl structures in both polyisoprene and polybutadiene since it was believed that vinyl groups adversely affected tire performance. Since natural rubber was 99.9% *cis*-1,4 structure and had superior properties, they believed that a 1,4 structure was necessary for acceptable physical properties. The addition of polar compounds to the lithium-catalyzed polymerization of butadiene changes the microstructure from the 90% *cis*-1,4 structure to a mixed *cis*-1,4 and *trans*-1,4 microstructure.

1. Microstructures of Polybutadiene

The conjugated structure of 1,3-butadiene gives it the ability to accept nucleophiles at both ends and distribute charge at both carbon 2 and 4. The initial addition of nucleophiles leads to transition states of π-allyl complexes in both anionic and transition-metal polymerizations.

It has been postulated that the syn π-allyl structure yields the *trans*-1,4 polymer, and the anti π-allyl structure yields the *cis*-1,4 polymer. Both the syn and anti π-allyl structures yield 1,2 units. In the formation of 1,2-polybutadiene, it is believed that the syn π-allyl form yields the syndiotactic structure, while the anti π-allyl form yields the isotactic structure. The equilibrium mixture of syn and anti π-allyl structures yields heterotactic polybutadiene. It has been shown (20–26) that the syndiotactic stereoisomers of 1,2-polybutadiene units can be made with transition-metal catalysts, and the pure 99.99% 1,2-polybutadiene (heterotactic polybutadiene) [26160-98-5] can be made by using organolithium compounds modified with bis-piperidinoethane (27). At present, the two stereoisomers of 1,2-polybutadiene that are most used commercially are the syndiotactic and the heterotactic structures.

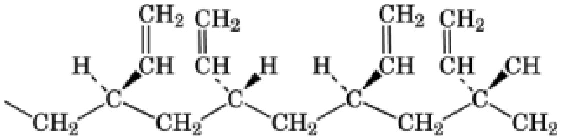
1.1. High Vinyl Polybutadiene

These 1,2 addition products are categorized into three main groups: syndiotactic, isotactic, and atactic 1,2-polybutadiene. The 1,2 vinyl products follow a stereospecific addition in which the chiral carbon carrying the pendent vinyl group leads to the formation of ldl, lll, or ddd configurations. The ldl structure is called syndiotactic polybutadiene, and the lll or ddd structures are called isotactic polybutadiene. A mixed structure (dldlldldl) is called atactic polybutadiene. Each of these structures gives polymers with unique physical, mechanical, and rheological properties.

1.1.1. Syndiotactic Polybutadiene

Syndiotactic polybutadiene is a unique material that combines the properties of plastic and rubber. It melts at high (150–220°C) temperatures, depending on the degree of crystallinity in the sample, and it can be molded into thin films that are flexible and have high elongation. The unique feature of this plastic-like material is that it can be blended with natural rubber. *cis*-1,4-Polybutadiene and the resulting blends exhibit a compatible formulation that combines the properties of plastic and rubber.

Syndiotactic polybutadiene was first made by Natta in 1955 (28) with a melting point of 154°C. Syndiotactic polybutadiene [31567-90-5]can be prepared with various melting points depending on its vinyl content and degree of crystallinity. The physical, mechanical, and rheological properties of the polymer are greatly affected by these parameters.



1.1.1.1. Preparation. There are several methods described in the literature using various cobalt catalysts to prepare syndiotactic polybutadiene (29–41). Many of these methods have been experimentally verified; others, for example, soluble organoaluminum compounds with cobalt compounds, are difficult to reproduce (30). A cobalt compound coupled with triphenylphosphine aluminum alkyls water complex was reported by Japan Synthetic Rubber Co., Ltd. (JSR) to give a low melting point ($T_m = 75 - 90°\mathrm{C}$), low crystallinity (20–30%) syndiotactic polybutadiene (32). This polymer is commercially available.

The addition of dienophile to cobalt compounds reduced with alkyl aluminum compounds has been reported (31); diethyl fumarate was used as modifier, and a high melting point syndiotactic polybutadiene ($T_m = 150°\text{C}$) was obtained. Preparation of a highly crystalline and high melting point syndiotactic polybutadiene has been reported by many investigators (32–36). The present authors have prepared a syndiotactic polybutadiene with a T_m of 200–210°C by adding carbon disulfide to a cobalt–aluminum alkyl catalyst. Increased yield and a highly crystalline material was developed at Firestone (38) using sulfur, nitrogen ligand, and cobalt compounds. Moreover, the use of carbon oxysulfide was found to give the same type of highly crystalline polymer (38, 42). The catalyst, based on cobalt complexed with polar compounds in the presence of reducing agent (trialkylaluminum) and carbon disulfide (CS_2), produced a highly crystalline syndiotactic polybutadiene. This process has been commercialized by Ube Industries Co., Ltd. (29). The Ube group proposed a mechanism for this polymerization which consists of a side-on coordination of the CS_2 to cobalt, anti-π-allyl growing end cisoid bidentate coordination of butadiene. This mechanism was based on an aluminum-free catalyst, $Co(C_4H_6)(C_8H_{13})–CS_2$.

An unusual method for the preparation of syndiotactic polybutadiene was reported by The Goodyear Tire & Rubber Co. (43); a preformed cobalt-type catalyst prepared under anhydrous conditions was found to polymerize 1,3-butadiene in an emulsion-type recipe to give syndiotactic polybutadienes of various melting points (120–190°C). These polymers were characterized by infrared spectroscopy and nuclear magnetic resonance (44–46). Both the Ube Industries catalyst mentioned previously and the Goodyear catalyst were further modified to control the molecular weight and melting point of syndio-polybutadiene by the addition of various modifiers such as alcohols, nitriles, aldehydes, ketones, ethers, and cyano compounds. The use of water as a co-catalyst in Ziegler-type polymerizations was first introduced in 1962 (47). The reaction kinetics and crystallinity of the resulting polymers measured by x-ray scattering has been studied (48–51).

1.1.1.2. Physical Properties. By using different catalysts and polymerization techniques, syndiotactic polybutadiene can be prepared with various melting points. An extensive review of high melting syndiotactic polybutadiene has been published (51). Two types of syndiotactic polybutadiene are most relevant to industrial applications; a high melting syndio-polybutadiene ($T_m = 190 - 216°\text{C}$) and a low melting syndio-polybutadiene ($T_m = 70 - 90°\text{C}$). The low melting type is commercially available from the Japan Synthetic Rubber Co. (JSR).

The physical properties of syndiotactic polybutadiene are controlled by its melting point, degree of crystallinity, and molecular weight. Typical differential scanning calorimetry (dsc) scans for various low melting syndiotactic polybutadienes are shown in Figure 1. Even though the 1,2 content of the polybutadienes differs by only 3%, the T_m varies from 71 to 105°C. The T_gs are all about $-10°\text{C}$. This implies that the melting point of the syndio-polybutadiene is dependent on the amount of amorphous structure embodied in the crystalline matrix rather than the vinyl content. Molecular weight also influences the melting point and glass-transition temperature. The molecular weight of the JSR material varies between 30,000 and 100,000. The higher molecular weight material has the highest melting point.

The physical properties of low melting point (60–105°C) syndiotactic polybutadienes commercially available from JSR are shown in Table 1. The modulus, tensile strength, hardness, and impact strength all increase with melting point. These properties are typical of the polymer made with a cobalt catalyst modified with triphenylphosphine ligand.

The stress–strain behavior of several low melting syndio-polybutadienes is similar to that of low density polyethylene. Increasing the melting point and crystallinity of the syndio-polybutadienes increases its modulus and brittle point. The polybutadienes with higher crystallinity and T_ms have higher moduli. The storage modulus of the low melting material is very similar to ethylene–vinyl acetate polymer, but lower than low density polyethylene. At low temperatures, syndiopolybutadiene has a higher storage modulus than either EVA films or LDPE (39).

High melting syndio-polybutadiene (T_m between 190–210°C) made with cobalt catalyst has different physical properties than the low melting material described previously. A typical dsc curve shows a sharp melting peak at 207°C. Annealing the polymer at 205°C for 12 h slightly increased the T_m to 212°C. The

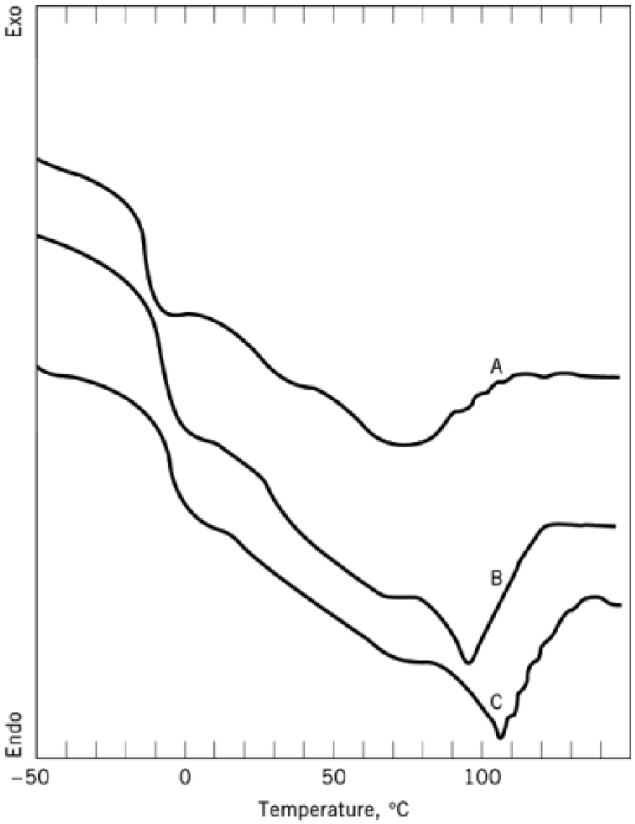


Fig. 1. Differential scanning calorimeter (dsc) curves of three grades of low melting syndiotactic 1,2-polybutadiene. A, 90% 1,2: T_m=71°C; B, 92% 1,2: T_m=95°C; C, 93% 1,2: T_m=105°C. Heating rate: 20°C/min.(Courtesy of the Japan Synthetic Rubber Co., RB product brochure.)

annealing did not significantly change the melting temperature, suggesting that the crystallites in the original sample were well ordered.

Typical polymerization conditions used to produce a syndiotactic 1,2-polybutadiene with a melting point of 206°C have been given (52). The dynamic storage modulus E' and loss modulus E'' have been plotted as a function of temperature for this high melting polymer ($T_m = 206°\text{C}$) (52). The peak in the E'' curve indicates a glass-transition temperature of $+40°\text{C}$. This means that this syndiotactic polybutadiene is highly crystalline and has a high vinyl content ($>95\%$).

Measurements of the mechanical properties of high melting syndiotactic polybutadiene compared to isotactic polypropylene indicate that syndio-polybutadiene has higher tensile strength at the breaking point, lower initial modulus, and lower distortion temperature than polypropylene. In addition, syndiotactic polybutadiene can be more easily cross-linked, functionalized, and cyclized due to its side-chain unsaturation as compared to polypropylene. Moreover, syndiopolybutadiene can be easily loaded with carbon fibers and graphite and at higher loadings.

1.1.2. Amorphous High 1,2-Polybutadiene

The increased emphasis on energy conservation puts pressure on the tire industry to produce a tire with low rolling resistance and better fuel economy. Tire designers, by changing the tire geometry and tread patterns,

Table 1. Physical Properties of Low Melting Syndiotactic 1,2-Polybutadiene

		Measured value			
Properties	Test method	JSR[a] RB805	JSR[a] RB810	JSR[a] RB820	JSR[a] RB830
density, g/cm^3	ASTM D1505 modify (at 20°C)	0.898	0.901	0.906	0.909
microstructure, % of 1,2 bonds	infrared spectrum	90	90	92	93
refractive index	ASTM D542	1.508	1.510	1.512	1.517
thermal properties, °C					
vicat softening point	ASTM D1525		39	52	68
brittle point	ASTM D746	−42	−40	−37	−35
melting point	ASTM D3418	59	71	95	105
tensile properties, 300% modulus, MPa[b]	ASTM D412	2.4	3.9	5.9	7.8
strength at break, MPa[b]		4.9	6.4	10.3	12.7
elongation at break, %		800	750	700	670
hardness	ASTM D2240				
Shore D		19	32	40	47
Shore A		70	82	95	99
izod impact strength, notched, (N·cm)/cm[c]	ASTM D256	21.6–22.6	—does not break—		
transmittance of parallel light[d], %	ASTM D1003	93	91	89	82
haze value[d], %	ASTM D1003	2.7	2.6	3.4	8.0
mold shrinkage[e], %	JSR method	2.3–3.3	0.7–0.9	0.3–0.5	0.3–0.6

[a] Japan Synthetic Rubber Co.; noncross-linked; melt flow index, 150°C, 2.160 *g* is 3 g/10 min for all grades.

[b] To convert MPa to kgf/cm^2, multiply by 10.2; to psi, multiply by 145.

[c] To convert (N·cm)/cm(J/m) to ftlbf/in., divide by 53.38.

[d] Values measured with 2 mm thickness sheet molded by injection molding machine set at cylinder temperature 150°C, mold temperature 20°C.

[e] 130°C medium speed injection molding; mold temperature 20°C; ASTM No. 1 dumb bells.

have produced only limited success. The compounding technologist using existing polymers such as natural rubber, emulsion, styrene–butadiene rubber, and *cis*-1,4-polybutadiene has been unable to simultaneously reduce rolling resistance and increase traction. Typically, a polymer with low rolling resistance also has low traction. Developing tread formulations for optimum traction and high resilience is paramount. However, in doing so many other tire properties are drastically affected. High tread modulus and hysteresis affect tire performance in traction, tread wear, and high resilience. A single-tread compound having single-hardness/hysteresis combinations cannot provide maximum performance in all tire-related properties simultaneously. High resilient (low hysteresis) tread rubber is desirable for reducing the lower rolling resistance tread compounds. The amount of energy which is lost or connected to heat is minimized thereby reducing tire rolling resistance. Whereas highly resilient tread compounds are desirable for reducing rolling resistance, they generally result in lower wet traction and poor tread resistance.

A goal for the synthetic polymer chemist is to molecularly engineer a polymer chain such as high vinyl polybutadiene to give low rolling resistance without compromising on wet grip and abrasion. The introduction of vinyl units into polybutadiene significantly changes its glass-transition temperature and physical properties. In this manner, the synthetic polymer chemist may be able to balance wet grip and fuel economy.

In recent years, high vinyl polybutadiene has become increasingly important to the tire industry. On a mid-size car, 7–10% of the fuel consumption can be attributed to rolling resistance losses from the tire. More than 50% of this tire energy loss comes from the tread. This makes a low hysteretic tread rubber very

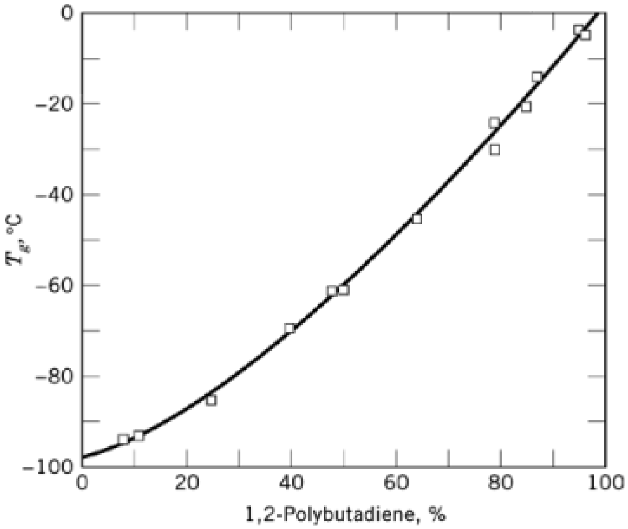


Fig. 2. T_g of polybutadiene vs 1,2 content.(Courtesy of the Goodyear Tire & Rubber Co.)

desirable as long as it maintains other important properties such as wet grip and tread wear. Amorphous, high vinyl polybutadiene is useful in tread formulations developed for energy conservation due to its low hysteresis and good wet grip characteristics. An amorphous, high 1,2-polybutadiene has been commercialized by the Nippon Zeon Co. under the trade names BR1240 and BR1245. These polymers showed better wet grip/rolling resistance behavior of butadiene rubbers having different vinyl contents. Rubber with 72% vinyl displayed a better compromise between rolling resistance and wet grip than customary rubbers due to the shift and rotation of the loss modulus pattern as a function of frequency.

1.1.2.1. Preparation. The preparation of amorphous high (99%) 1,2-polybutadiene was first reported in 1981 (27). The use of a heterocyclic chelating diamine such as dipiperidine ethane in the polymerization gave an amorphous elastomeric polymer of 99.9% 1,2 units and a glass-transition temperature of $+5^{\circ}\mathrm{C}$. In a previous description (53, 54) of the use of a chelating diamine such as *N,N,N′,N′*;-tetramethylethylene diamine, an 80% 1,2-polybutadiene with a glass-transition temperature of $-30^{\circ}\mathrm{C}$ was produced.

Several reports in the literature describe the preparation and characterization of low, medium, and high vinyl polybutadienes (55–69). Each of these references used polar modifiers including chelating diamines, oxygenated ether compounds, acetals, ketals, and compounds of similar structures (56–64).

The random spatial arrangement of vinyl groups (ie, lddldlldl) in atactic polybutadiene results in an amorphous, rubbery polymer whose glass-transition temperature is a function of vinyl content (Fig. 2. The vinyl content of polybutadiene is controlled by the ratio of the polar modifier to the active lithium catalyst as well as the polymerization temperature (70–72). Raising the modifier/lithium ratio increases the vinyl content and T_g of the polybutadiene (Fig. 3). Above a ratio of about 2:1, additional modifier has no effect on the polymer microstructure. At a 2:1 modifier:lithium ratio, the vinyl content decreases with increasing polymerization temperature up to about 60°C (Fig. 4). Increasing the polymerization temperature above 60°C does not further reduce the vinyl content. By controlling the polymerization temperature and modifier ratio, the synthetic polymer chemist can prepare a variety of polymer microstructures.

1.1.2.2. Properties of Amorphous High Vinyl Polybutadiene. The microstructural control described is possible only with living anionic polymerizations of conjugated diene monomers such as 1,3-butadiene, isoprene, and 2,3-dimethylbutadiene, and in copolymerizations of conjugated diene monomers and vinylaromatics to prepare solution styrene–butadiene copolymers. This microstructural variation can give polymers with a wide

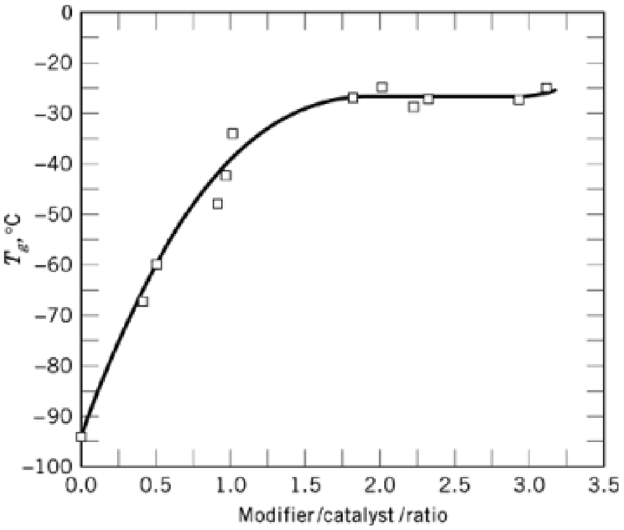


Fig. 3. Effect of modifier ratio on polymer T_g.(Courtesy of the Goodyear Tire & Rubber Co.)

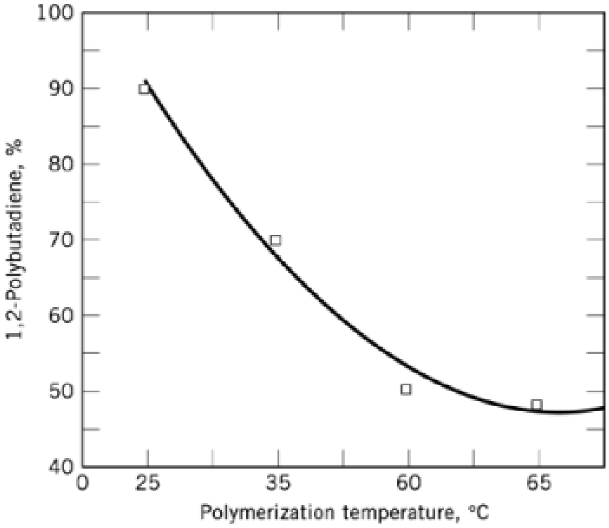


Fig. 4. Effect of polymerization temperature on vinyl content at a 2:1 modifier:lithium ratio.(Courtesy of the Goodyear Tire & Rubber Co.)

range of glass-transition temperatures. Using this method, one can develop a single polymer in which the desired combination of physical properties can be obtained. For example, tire properties such as wet grip, hysteresis, and wear can be controlled by the introduction of vinyl groups to polybutadiene. A low vinyl polybutadiene (10–30% 1,2; T_g between -70 and $-85°C$) has good wear and excellent fuel economy but poor traction. The high vinyl polymer (80–95% 1,2; T_g between -10 and $-30°C$) has excellent traction and fuel economy but poor wear properties. By manipulating the polymer structure, one can prepare a 70% vinyl polybutadiene with a T_g of $-40°C$ that has the optimum balance of traction, wear, and rolling resistance. The effect of polymer microstructure on physical properties is depicted in Figure 5.

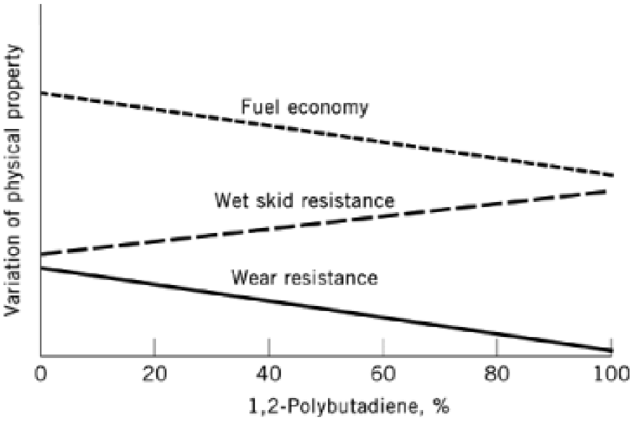


Fig. 5. Effect of 1,2-polybutadiene level on tire physical properties.

Based on this variety of properties, amorphous polybutadiene has found a niche in the rubber industry. Moreover, it appears that the anionically prepared polymer is the only polymer that can be functionalized by polar groups. The functionalization is done by using aromatic substituted aldehydes and ketones or esters. Functionalization has been reported to dramatically improve polymer-filler interaction and reduce tread hysteresis (70–73).

1.2. cis-1,4-Polybutadiene

There are numerous references in the literature on the preparation of *cis*-1,4-polybutadiene (74–83). These authors have used transition metals in the presence of a reducing agent such as organoaluminum compounds or its chloride or hydride derivatives. In many cases nickel, cobalt, iron, or vanadium have been used in combination with organometallics of Groups I, II, or III. The resulting polybutadienes usually have *cis*-1,4 contents between 90–98%. The molecular weights of these polymers are very high, and usually a transfer agent such as internal or terminal olefins is employed (75–80).

For example, *cis*-1,4-polybutadiene has been made using a titanium halide such as $TiCl_4$, $TiBr_4$, or TiI_4. The most useful combination is $TiCl_4/(C_2H_5)_3Al$. The highest *cis*-1,4 content ($>90\%$) is obtained from TiI_4. The combination of $TiI_4/(C_2H_5)_3Al$ has been successfully scaled up to give a gel-free, $>90\%$ *cis*-1,4-polybutadiene. This catalyst is heterogeneous, and requires special equipment to make a fine catalyst dispersion. Another system that has also been scaled up commercially is the cobalt system. This heterogeneous catalyst is homogeneously prepared using the cobalt salt of octanoate or napthenates, or complexed with pyridine. The cobalt system employs both aluminum alkyls and aluminum sesquichlorides (80–86). Cobalt systems usually produce polybutadienes with very high molecular weights. A chain-transfer agent such as ethylene, hydrogen, or methylallene is usually added to control the molecular weight.

Another transition-metal system that gives greater than 90% *cis*-1,4 content is based on nickel. This nickel system is currently used commercially to produce over 450,000 kg per day of *cis*-1,4-polybutadiene. The catalyst was first developed based on the BF_3 etherate system reduced with trialkylaluminum. The BF_3 etherate system became fully commercial in the late 1970s, and was used until the early 1980s. At that time, the system was completely modified using hydrogen fluoride to give a gel-free, 98% *cis*-1,4-polybutadiene with a controlled molecular weight and broad molecular weight distribution (87–94).

The unique advantage of the nickel system is that it can produce either structures of *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, or a mixture of both depending on the reducing agent and the co-catalyst used. For example, chloride catalyst yields *cis*-1,4-polybutadiene, whereas bromide or iodide yields *trans*-1,4-polybutadiene. The counterion also has an effect on the polymer microstructure. A 50/50 *cis*-1,4/*trans*-1,4-polybutadiene has been prepared using a carboxylic counterion (95–105).

1.3. trans-1,4-Polybutadiene

trans-1,4-Polybutadiene can be prepared using transition-metal catalysts or a nontransition-metal catalyst system based on Group I and II metals. The transition metals used include titanium, vanadium, chromium, rhodium, iridium, cobalt, and nickel (106–111).

The *trans*-1,4-polybutadiene made by transition-metal catalysis (112, 113) is a resin-like material that has two melting temperatures, 50 and 150°C. This solid resinous material has not found much application because it is difficult to stabilize. However, the same type of polymer was prepared using a Group I metal alkoxide in combination with organometallics of the same group. For example, previous work (114, 115) showed that reduction of potassium alkoxide with either organolithium or organomagnesium gave a 90–99% *trans*-1,4 structure with melting points of 50 and 175°C. This resinous, crystalline polymer was insoluble in hexane, and was isolated in quantitative yield. It can be isomerized to give a rubbery material.

A *trans*-1,4-polybutadiene that is useful as a tire rubber and can be stabilized and processed using conventional equipment has been made using an alkoxide of group II reduced with organolithium or organomagnesium compounds in the presence of lithium alkoxide salts and aluminum alkyls (116–123). This homogeneous catalyst system gives a rubbery, *trans*-1,4-polybutadiene with controlled molecular weight and a T_m of about +30 to +40°C. The polymer crystallizes upon stretching, and shows 30% crystallinity by wide angle x-ray scattering analysis. The broad crystalline melt peak observed by dsc suggests that a wide distribution of crystallite sizes exist in a rubbery matrix. The microstructure of this polymer based on ^{13}C-nmr shows 80% *trans*-1,4, 17% *cis*-1,4, and 3% 1,2. This polymer is different than the ultrahigh mol wt polybutadiene made with Alfin catalyst, since it is soluble in hydrocarbon solvents such as hexane (125–131). The polymer made by the well-known Alfin catalyst (132–134) gives an ultrahigh mol wt polybutadiene with a broad T_m at +40°C, and a microstructure of 70% *trans*-1,4 and 30% 1,2 units. X-ray diffraction analysis shows about 25–30% crystallinity.

1.4. Mixed Microstructure Polybutadiene

An amorphous polybutadiene of 10% vinyl, 35% *cis*-1,4, and 55% *trans*-1,4 structure can be made with a living anionic catalyst (135–139). This polymer is currently sold by Firestone under the name of Diene, and by Asahi under the name of Taktene. It has poor green strength, but shows excellent physical properties when compounded in a tire tread. This tread rubber, made in a living polymerization using a lithium catalyst, shows excellent tread wear as well as low hysteresis. Moreover, this type of polymer can be functionalized since the end of the polymer chain carries an active carbon metal linkage. This carbon-bound metal has been functionalized with ketones, aldehydes, acid chlorides, and metal halides of silicon and tin. Using silicon tetrachloride to couple the polybutadiene gives a polymer with a molecular weight four times that of the original polymer, and improves its hysteretic properties. Moreover, it has been claimed that it also shows better tread wear due to improved carbon black dispersion without a loss in hysteresis. There are claims in the literature that tin-coupled polybutadiene has lower hysteresis due to the formation of carbon–tin bonds that help break up the carbon black agglomerates into smaller aggregates; this results in improved carbon black dispersion (140–146).

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