PBD, *cis* *cis*-1,4-polybutadiene

PARAMETER	UNIT	VALUE	REFERENCES
GENERAL			
Common name	-	*cis*-1,4-polybutadiene	
CAS name	-	butadiene rubber, of cis-1,4-configuration	
Acronym	-	*cis*-PBD	
CAS number	-	9003-17-2	
HISTORY			
Person to discover	-	Smith, D R; Zielinski, R P	Smith, D R; Zielinski, R P, US Patent 3,976,630, Phillips Petroleum, Aug. 24, 1976.
Date	-	1976	
Details	-	emulsion polymerization	
SYNTHESIS			
Monomer(s) structure	-	$H_2C=CHCH=CH_2$	
Monomer(s) CAS number(s)	-	106-99-0	
Monomer(s) molecular weight(s)	dalton, g/mol, amu	54.09	
Monomer(s) expected purity(ies)	%	min. 90 wt% (typical 99.5 wt%)	
Monomer ratio	-	100%	
Formulation example	-	see in the method of synthesis	
Method of synthesis	-	a dry solution of butadiene in hexane (35 wt%) is first charged under nitrogen into reactor, followed by the addition of dry hexane. The reaction medium was heated up to the stated reaction temperature (50-100°C) and catalyst was added. The monomer concentration in the reaction medium varies from 0.56 to 1.05 mol/l. Polymerization is terminated by adding a hexane solution of 2,6-di-trans-butyl-4-methmethylphenol (BHT) @ 50 wt% and stabilized by adding a hexane solution of TNPP @ 10 wt%. The polymer is coagulated in hot water under vigorous agitation and dried in an oven at 60°C.	Pires, N M T; Coutinho, F M B; Costa, M A S, Eur. Polym. J, 40, 2599-2603, 2004.
Temperature of polymerization	°C	70-8	Pires, N M T; Coutinho, F M B; Costa, M A S, Eur. Polym. J, 40, 2599-2603, 2004.
Time of polymerization	h	5	Pires, N M T; Coutinho, F M B; Costa, M A S, Eur. Polym. J, 40, 2599-2603, 2004.
Pressure of polymerization	Pa	atmospheric (typical) or higher	
Optimum polymerization conditions	-	monomer concentration 22%, reaction time 3.3 h and reaction temperature 42°C for the specified catalyst system	Maiti, M; Srivastava, V K; Shewale, S; Jasra, R V; Chavda, A; Modi, S, Chem. Eng. Sci., 107, 256-65, 2014.
Catalyst	-	triethylaluminum+titanium tetraiodate; also neodynium catalyst for ultrahigh cis-PB; cobalt complexes; optimum catalyst formulation was observed to be 1,3-butadiene/neodymium octanoate, diethylaluminum chloride/neodymium octanoate and triethylaluminum/neodymium octanoate molar ratio of 902.88, 1.74 and 27.51, respectively	Schonema, D P; Stachowiak, R W, US Patent 4,020,255, Goodyear Tire and Rubber Company, 1977; Rodriguez Garraza, A L; Sorichetti, P; Marzocca, A J; Matteo, C L; Monti, G A, Polym. Test., in press, 2011; Gong, D; Wang, B; Cai, H; Zhang, X; Jiang, L, J. Organometallic Chem., 696, 1584-90, 2011; Maiti, M; Srivastava, V K; Shewale, S; Jasra, R V; Chavda, A; Modi, S, Chem. Eng. Sci., 107, 256-65, 2014.
Yield	%	above 95% of *cis*-isomer	Schonema, D P; Stachowiak, R W, US Patent 4,020,255, Goodyear Tire and Rubber Company, 1977.

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Heat of polymerization	J g^{-1}	1350-1442	Roberts, D E, J. Res. Natl. Bur. Std, 44, 221-7, 1950.
Number average molecular weight, M_n	dalton, g/mol, amu	5,000-152,000	
Mass average molecular weight, M_w	dalton, g/mol, amu	56,500-817,000	Kariyo, S; Gainaru, C; Schick, H; Brodin, A; Novikov, V N; Roessler, E A, Phys. Rev. Lett., 97, 207803,1-4, 2006.
Polydispersity, M_w/M_n	-	2.0-3.8	
Molar volume at 298K	cm^3 mol^{-1}	calc.=59.8; 53.5 (crystalline); 60.7 (amorphous); exp.=60.7	
Van der Waals volume	cm^3 mol^{-1}	37.1 (crystalline); 37.5 (amorphous); exp.=37.84	
STRUCTURE			
Crystallinity	%	18-24	Di Lorenzo, M L, Polymer, 50, 578-84, 2009.
Cell type (lattice)	-	monoclinic	
Cell dimensions	nm	a:b:c=0.853:0.816:1.266	
Unit cell angles	degree	β=83.33	
Tacticity	%	*cis*: 95-98.4%	Di Lorenzo, M L, J. Appl. Polym. Sci., 116, 1408-13, 2010.
Dielectric moment	Debye	0.33 (*cis*); 0.5 (vinyl)	
Entanglement molecular weight	dalton, g/mol, amu	calc.=1,581; 1,844-2,000	Kariyo, S; Gainaru, C; Schick, H; Brodin, A; Novikov, V N; Roessler, E A, Phys. Rev. Lett., 97, 207803,1-4, 2006.
Isothermal crystallization temperature	°C	-26	
COMMERCIAL POLYMERS			
Some manufacturers	-	Lanxess	
Trade names	-	Buna	
PHYSICAL PROPERTIES			
Density at 20°C	g cm^{-3}	0.890-0.915	
Color	-	colorless to white	
Refractive index, 20°C	-	calc.=1.502-1.5188; exp.=1.516-1.605	
Molar polarizability	cm^3 x 10^{-25}	71.4	
Odor	-	rubber-like	
Melting temperature, DSC	°C	1	
Thermal expansion coefficient, 23-80°C	$°C^{-1}$	1.5-6.7E-4	
Thermal conductivity, melt	W m^{-1} K^{-1}	calc.=0.1788; exp.=0.22	
Glass transition temperature	°C	calc.=-72 to -103.0; exp.=-99 to -106; -102 (*cis*) and -83 (*trans*)	Di Lorenzo, M L, Polymer, 50, 578-84, 2009.
Specific heat capacity	J K^{-1} kg^{-1}	1,850-1,950	Di Lorenzo, M L, Polymer, 50, 578-84, 2009.
Heat of fusion	kJ mol^{-1}	2.51	

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Hansen solubility parameters, δ_D, δ_P, δ_H	$MPa^{0.5}$	17.5, 2.3, 3.4; 17.3, 2.25, 3.42	
Interaction radius		6.5; -	
Hildebrand solubility parameter	$MPa^{0.5}$	16.2-18.0	
Surface tension	mN m^{-1}	calc.=33.5-39.8; exp.=32.0	
Dielectric constant at 50 Hz/1 MHz	-	2.3/-	
Permeability to nitrogen, 25°C	cm^3 cm cm^{-2} s^{-1} Pa^{-1} x 10^{12}	1.44	
Diffusion coefficient of nitrogen	cm^2 s^{-1} $x10^6$	1.5	Gestoso, P; Meunier, M, Molecular Simulations, 34, 10-15, 1135-41, 2008.
Diffusion coefficient of oxygen	cm^2 s^{-1} $x10^6$	1.1-3.0	Gestoso, P; Meunier, M, Molecular Simulations, 34, 10-15, 1135-41, 2008.
Contact angle of water, 20°C	degree	95-97	
Surface free energy	mJ m^{-2}	45.9	
MECHANICAL & RHEOLOGICAL PROPERTIES			
Tensile strength	MPa	16.2-20	
Tensile stress at yield	MPa	8.9-9.3	
Elongation	%	450-620	
Tear strength	kN m^{-1}	36.3-69.6	
Abrasion resistance (ASTM D1044)	mg/1000 cycles	41-44	
Poisson's ratio	-	calc.=0.432	
Compression set, 22h 70°C	%	13-15	
Shore A hardness	-	64-88	
Mooney viscosity	-	33-55	
CHEMICAL RESISTANCE			
Acid dilute/concentrated	-	not resistant	
Alcohols	-	resistant	
Alkalis	-	not resistant	
Aromatic hydrocarbons	-	not resistant	
Esters	-	not resistant	
Halogenated hydrocarbons	-	not resistant	
Θ solvent, Θ-temp.=10.3, -1, 35.5, 144°C	-	diethyl ketone, n-heptane, n-propyl acetate, propylene oxide	
Good solvent	-	higher ketones, higher aliphatic esters, hydrocarbons, THF	
Non-solvent	-	alcohol, dilute acids, dilute alkalies, nitromethane, propionitrile, water	
FLAMMABILITY			
Ignition temperature	°C	200	

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WEATHER STABILITY			
Products of degradation	-	hydroperoxides, carbonyls, H_2O, chain scissions, crosslinks, carboxyl groups	
Stabilizers	-	UVA: 2(2'-hydroxy-5-methylphenyl)benzotriazole; Screener: carbon black; HAS: bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-2-n-butyl-2-(3,5-di-tert-butyl-4-hydroxy-benzyl) malonate; Phenolic antioxidants: phenol, 4-methyl-, reaction products with dicyclopentadiene and isobutene; 2,6,-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5,-triazine-2-ylamino) phenol; 2-(1,1-dimethylethyl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl] methyl-4-methylphenyl acrylate; isotridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate; 3,5-bis(1,1-dimethyethyl)-4-hydroxy-benzenepropanoic acid, C13-15 alkyl esters; 2,2'-isobutylidenebis(2,4-dimethylphenol); Amine: nonylated diphenylamine; Thiosynergist: 2,2'-thiobis(6-tert-butyl-4-methylphenol); 4,6-bis(octylthiomethyl)-o-cresol	
BIODEGRADATION			
Typical biodegradants	-	horseradish peroxidase	Enoki, M; Kaita, S; Wakatsuki, Y; Doi, Y; Iwata, T, Polym. Deg. Stab., 84, 321-26, 2004.
TOXICITY			
NFPA: Health, Flammability, Reactivity rating	-	1/1/0	
Carcinogenic effect	-	not listed by ACGIH, NIOSH, NTP	
PROCESSING			
Typical processing methods	-	blow molding, extrusion, injection molding, mixing, molding, vulcanization	
Additives used in final products	-	Fillers: carbon black, china clay, fly ash, mica, nano-calcium carbonate, nano-magnesium hydroxide, zinc oxide; Plasticizers: chlorinated paraffins, dioctyl sebacate, dibuthyl phthalate, dioctyl phthalate, paraffinic, aromatic, or naphthenic mineral oils, polyisobutylene; Antiblocking: diatomaceous earth; Release: liquid polybutadiene; Slip: erucamide+stearamide	
Applications	-	buffer springs, conveyor belts, golf balls, hoses, industrial flooring, modification of other polymers (e.g., HIPS and ABS), rubber pads for ballastless track, rubberized cloth, seals and gaskets, tires	
Outstanding properties	-	resiliency	
BLENDS			
Suitable polymers	-	NR, PE, PS	
ANALYSIS			
FTIR (wavenumber-assignment)	cm^{-1}/-	725 (*cis*-1,4), 910 (vinyl-1,2), and 965 (*trans*-1,4)	