

What are Polyisobutylene and Butyl Rubber? (Executive Summary)

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Polyisobutylene (PIB) and butyl rubber (IIR) belong to a class of materials called polymers (*i.e. poly* = many *mers* = units) or macromolecules (*e.g. macro* = large molecules).¹ Polymers are large molecules that are built from the chemical linking of smaller building blocks typically referred to as monomers. PIB (**1**) is a homopolymer of isobutylene (*i.e.* a polymer built completely of isobutylene units {Figure 1}) whereas butyl (**2**) is a copolymer of isobutylene and isoprene (*i.e.* a polymer built of isobutylene and isoprene units {Figure 1}).² Butyl rubber is

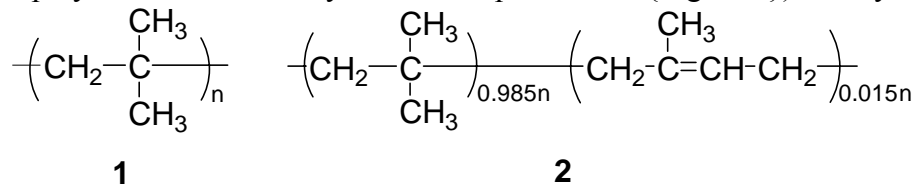


Figure 1. Repeat Units for PIB (1) and Butyl (2).

consists primarily of isobutylene (*ca* 98.5 mol %) and minor amounts of isoprene (*ca* 1.5 mol %). Polymerization of isoprene results in the incorporation of an alkene (*i.e.* double bond or unsaturation) into the polymer chain. These double bonds serve as crosslinking sites (*i.e.* sites where one polymer chain can be chemically linked to another). Vulcanization of the butyl copolymers results in the formation of a network structure in the form of a crosslinked rubber (Figure 2). In this case every butyl polymer chain is linked to each other to form one macroscopic molecule (*e.g.* the inner tube is actually one molecule). As such butyl is a *thermoset* polymer and once vulcanized it cannot be reformed into a new shape. PIB is a *thermoplastic* polymer and can be reshaped by application of heat/pressure since none of the individual PIB chains are chemically linked together.

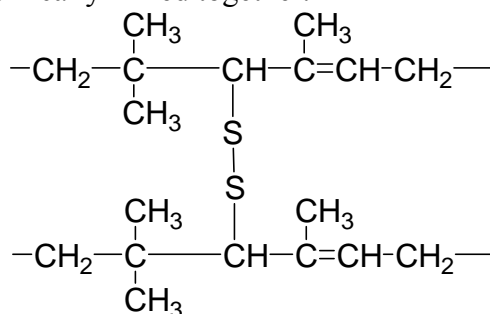
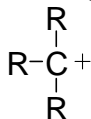


Figure 2. Example Crosslink of Sulfur Vulcanized Butyl.

The Basics of Carbocationic Polymerization

The chemical structure of a monomer determines the exact way or mechanism by which the linking reaction operates during the formation of a particular polymer. In the case of PIB and butyl the mechanism involves *carbocationic* intermediates (*i.e.* carbon species that have a deficiency of electrons giving them a positive charge {Figure 3}). This deficiency of electrons



R = unspecified substituent

Figure 3. Generic Structure for a Carbocation.

makes carbocations extremely reactive and highly acidic. They will literally react with the weakest of bases (*e.g.* isobutylene monomer) under reaction times of less than one nanosecond (*i.e.* one billionth of a second). Polymerization begins with an initiating event that can occur in a

variety of ways; all of which ultimately generate a carbocation. This process is termed *initiation* and each carbocation formed during this process has the ability to generate one or more polymer chain(s) (Figure 4). Under ideal conditions each carbocation formed during initiation gives rise

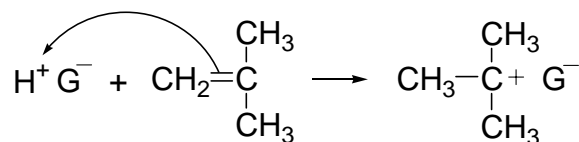


Figure 4. Initiation by Protonation.

to only one polymer chain; however, due to side reactions (*e.g.* chain transfer, termination) this is not always the case. Monomer units are then connected by successive addition of monomer to the carbocation resulting in growth and simultaneous regeneration of the carbocationic chain-end (Figure 5). This process is termed *propagation* and can occur repetitively thousands of times in

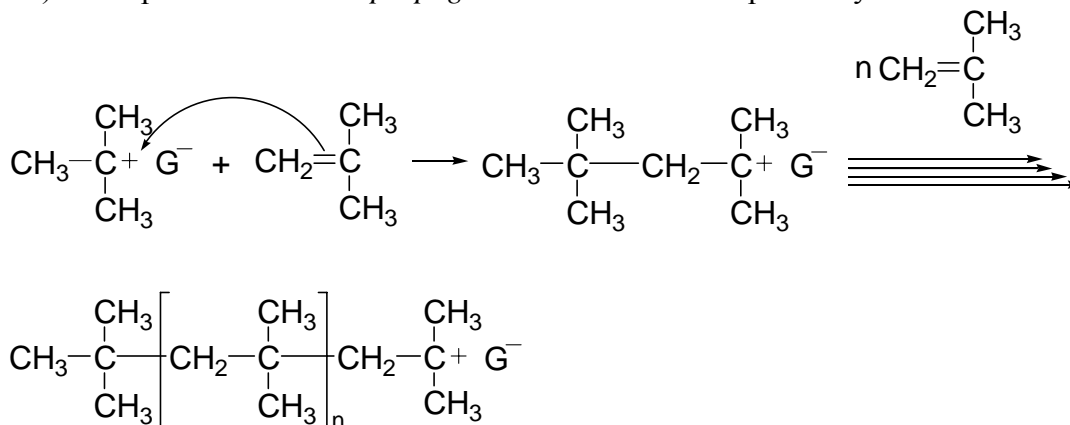


Figure 5. Propagation.

an extremely short period of time (*ca* < 1 second). Growing polymer chains can undergo complex reactions collectively known as *chain transfer* (Figure 6). The net result of chain

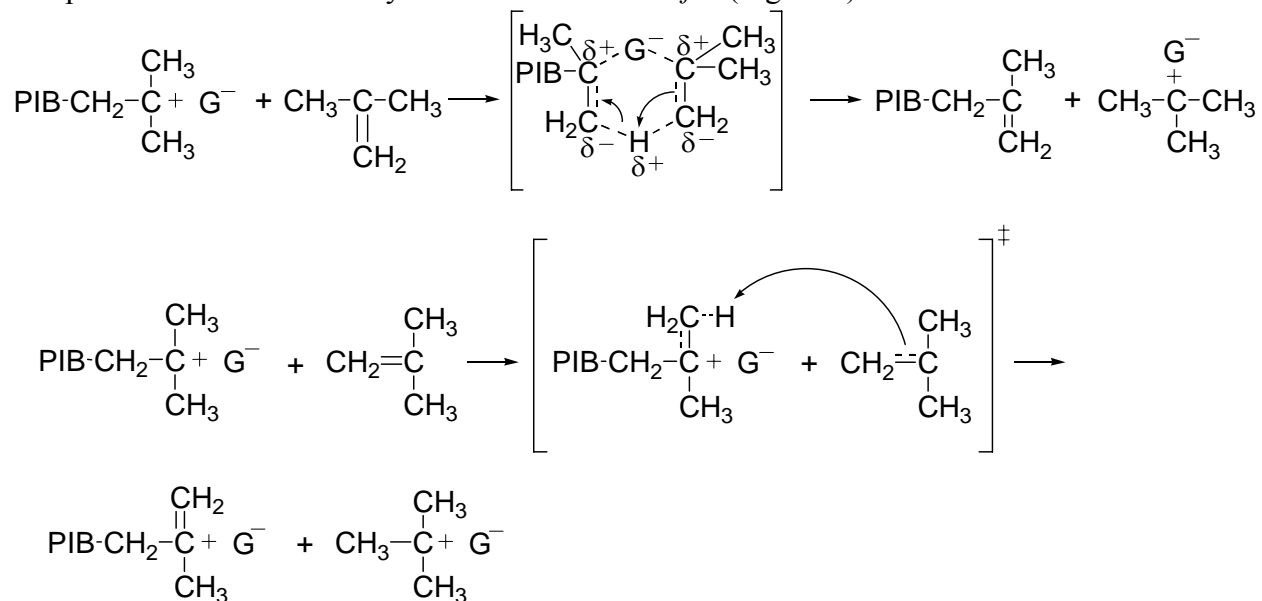


Figure 6. Counteranion Assisted Chain Transfer and Spontaneous Chain Transfer.

transfer is that a growing polymer chain is transformed into a dead chain with concomitant production of a new active carbocation that can initiate growth of a new polymer chain. The

final main reaction that can occur is transformation of a growing polymer chain into a dead polymer chain, a process referred to as *termination* (Figure 7). Termination involves the reaction

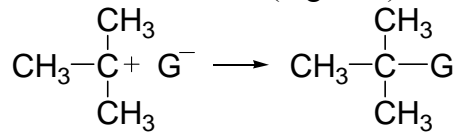


Figure 7. Termination by Collapse of an Ion Pair.

of a carbocation with another species in such a manner as to generate products incapable of initiating the growth of new polymer chains.

Uses and Market Data for PIB and Butyl Rubber

Depending on the number average molecular weight (\overline{M}_n) physical properties for PIBs can range from liquids to semiliquids and solids. PIBs have excellent stability to a wide range of chemicals and are soluble in a number of hydrocarbons and chlorohydrocarbons. They have a low glass transition temperature, low specific thermal conductivity, low water permeability, and high dielectric strength. Because they do not corrode metals or leave carbon residues when volatilized or depolymerized low \overline{M}_n PIBs are useful as lubricants, additives, and viscosity modifiers. Uses for higher \overline{M}_n PIBs include sealants, and adhesives. Traditional methods^{2a} for the preparation of high molecular weight PIBs ($\overline{M}_n > 10^5 \text{ g mol}^{-1}$) require polymerization temperatures $\leq -100 \text{ }^\circ\text{C}$ in order to reduce chain transfer to an acceptable level. In some cases^{2b-f} (processes using AlCl_3) toxic solvents (*e.g.* methyl chloride) are required for polymerization; strict regulations prohibit the building of new or expansion of existing plants that require such materials. BASF is the largest manufacturer of PIBs (10^6 metric tons year⁻¹ with costs ranging $\$0.8 \text{ kg}^{-1}$ for low \overline{M}_n grades and $\$1.7\text{-}2 \text{ kg}^{-1}$ for medium to high \overline{M}_n grades).³ Low \overline{M}_n PIBs bearing a high ($> 80 \%$) percentage of terminal unsaturation (*i.e.* reactive PIBs) are very desirable as lubrication additives but a cost effective, non-polluting system for their production has not been disclosed.^{2f,4}

Vulcanized butyl has the lowest gas and moisture permeability of all elastomers, excellent heat/ozone resistance, and high damping properties.^{2f-i} The main use of butyl is in tire-curing bladders and inner tubes. Commercial processes for the manufacture of butyl are costly and detrimental to the environment as they operate at temperatures $\leq -100 \text{ }^\circ\text{C}$ and require the use of toxic methyl chloride.^{2f-i} Legislation designed to protect the environment prevents the expanded use of methyl chloride in such processes. Currently $> 760,000$ metric tons of butyl is produced each year at a price of $\$2.8\text{-}3 \text{ kg}^{-1}$.^{2f,5} Exxon and Lanxess are the major manufacturers of butyl rubber. Uses for butyl rubber on a percentage basis include:

1. Tires, tubes and other pneumatic products = 80 %
2. Automotive mechanical goods = 9 %
3. Adhesives, caulks and sealants = 6 %
4. Pharmaceutical = 4 %
5. Miscellaneous = 1 %

References

1. Two good general references for polymer science are: (a) Odian, G. *Principles of Polymerization*; 3rd Ed.; John Wiley & Sons, Inc.: New York, 1991. (b) Billmeyer, F. W., Jr. *Textbook of Polymer Science*; 3rd Ed.; John Wiley & Sons, Inc.: New York, 1984.
2. (a) Otto, M.; Müller-Cunradi, M. Ger. Patent 641,284 (1931). (b) Güterbock, H. *Polyisobutene*, Springer Verlag, Berlin, 1959. (c) Immel, W. *Polyisobutene* in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B.; Haskins, S.; Schulz, G. Eds.; VCH Publishers: Weinheim; 1992; Vol. A21, pp. 555-561. (d) Kennedy, J.P.; Marechal *Carbocationic Polymerization*, Wiley-Interscience, New York; 1982; Chap. 10. (e) Kresge, E. N.; Schatz, R. H.; Wang, H-C. *Isobutene polymers* in *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Elvers, B.; Haskins, S.; Schulz, G. Eds.; Wiley-Interscience: New York; 1987; Vol. 8, pp. 423-448. (f) Vairon, J. P.; Spassky, N. in *Cationic Polymerization*; Matyjaszewski, K. Ed.; Marcel Dekker: New York, 1996; p. 683-704. (g) Thomas, R. M.; Sparks, W. J. U.S. Patent 2,356,128 (1944). (h) Duffy, J.; Wilson, G.J. *Synthesis of butyl rubber by cationic polymerization* in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B.; Haskins, S.; Russey, W.; Schulz, G. Eds.; VCH Publishers: Weinheim; 1993; Vol. A23, pp. 288-294. (i) Duffy, J.; Wilson, G.J. *Halobutyl rubber* in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B.; Haskins, S.; Russey, W.; Schulz, G. Eds.; VCH Publishers: Weinheim; 1993; Vol. A23, pp. 314-318.
3. Marsalko, T. (BASF) *personal communication*, **2005**.
4. (a) Rath, H. P.; Hahn, D.; Sandrock, G.; Deyck, F.; Straeten, B. V.; Vree, E. D. US Patent 6,753,389 (2004). (b) Nolan, J. T., Jr.; Chafetz, H. US Patent 3,024,226 (1962). (c) Nolan, J. T., Jr.; Chafetz, H. US Patent 3,166,546 (1965). (d) Vierle, M.; Schön, D.; Bohnenpoll, M.; Kühn, F. E.; Nuyken, O. CA Patent 2,421,688 (2003). (e) Guerrero, A. Kulbaba, K. Bochmann, M. *Macromolecules* **2007**, *40*(12), 4124-4126.
5. Kirschner, M. *Chem. Market. Rep.*, **2005**, June 6-15, 34.