Objectives

After completing this section, you should be able to

1. show that the polymerization of a diene, such as 1,3-butadiene or isoprene (2-methyl-1,3-butadiene), can result in the formation of either a cis or trans polymer.
2. draw the structure of natural rubber.
3. explain, briefly, the process of vulcanization.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- cross-link
- vulcanization

Study Notes

Natural rubber is formed from the isoprene monomer and has Z stereochemistry. The E polymer gutta-percha also occurs naturally, but is more brittle than rubber. Uses of this thermoplastic include dentistry, electrical insulators and the covering on golf balls.

cis- and trans-polyisoprene chains

Before 1839, the uses of natural rubber were somewhat limited. It became sticky in summer, hardened and cracked in winter, and was susceptible to attack by a variety of solvents. Charles Goodyear became interested in rubber in 1831, and bought the Eagle India Rubber Company of Woburn, Massachusetts, in 1838. In January of 1839, Goodyear accidentally placed a sample of rubber that had been mixed with sulfur and lead(II) oxide on a hot stove; the result was a product similar to charred leather, which did not melt below 138°C. Goodyear was granted a U.S. patent for his process (called vulcanization) in June of 1844. The story of vulcanization is an example of how major scientific and technological advances are often brought about as a result of an accidental discovery.

Notice that in the vulcanization process, the sulfur bridges are attached to allylic carbon atoms which connect the long Z polymer chains of rubber.

sulfur bridges in vulcanized rubber polymer chains

Vulcanized rubber

The amount of sulfur used in the vulcanization process will depend on the rigidity required in the product. For example, about 5% sulfur is used when producing rubber for rubber bands; about 30% sulfur is used when making rubber for use in battery casings. There are several characteristics of dienes and rubbers that you should recognize. First, be aware of the similarity between the polymerization of a diene and the 1,4-addition reactions of dienes. Second, recognize the similarity between a vulcanized rubber and a peptide containing cysteine cross-links. Third, be aware that as natural rubber contains double bonds, it will display some of the properties of simple alkenes.
The 1,4 polymerization of 1,3-butadiene shown in the reading produces the \textit{trans} form of polybutadiene. However, it should be noted that the \textit{cis} form shown here can also be formed.

\textbf{cis form of polybutadiene}

\textit{cis}-polbutadiene

Conjugated dienes (alkenes with two double bonds and a single bond in between) can be polymerized to form important compounds like rubber. This takes place, in different forms, both in nature and in the laboratory. Interactions between double bonds on multiple chains leads to cross-linkage which creates elasticity within the compound.

\begin{center}
\textbf{Polymerization of 1,3-Butadiene}
\end{center}

For rubber compounds to be synthesized, 1,3-butadiene must be polymerized. Below is a simple illustration of how this compound is formed into a chain. The 1,4 polymerization is much more useful to polymerization reactions.

\begin{center}
\textbf{1,2-Polymerization of 1,3-Butadiene}
\end{center}

\begin{center}
\textbf{1,4-Polymerization of 1,3-Butadiene}
\end{center}

Above, the green structures represent the base units of the polymers that are synthesized and the red represents the bonds between these units which form these polymers. Whether the 1,3 product or the 1,4 product is formed depends on whether the reaction is thermally or kinetically controlled.

\begin{center}
\textbf{Natural Rubber}
\end{center}

Natural rubber is an addition polymer that is obtained as a milky white fluid known as latex from a tropical rubber tree. Natural rubber is from the monomer isoprene (2-methyl-1,3-butadiene), which is a conjugated diene hydrocarbon as mentioned above. In natural rubber, most of the double bonds formed in the polymer chain have the $Z$ configuration, resulting in natural rubber's elastomer qualities.

Charles Goodyear accidentally discovered that by mixing sulfur and rubber, the properties of the rubber improved in being tougher, resistant to heat and cold, and increased in elasticity. This process was later called vulcanization after the Roman god of fire. Vulcanization causes shorter chains to cross link through the sulfur to longer chains. The
development of vulcanized rubber for automobile tires greatly aided this industry.

**Synthetic Rubber**

The most important synthetic rubber is Neoprene which is produced by the polymerization of 2-chloro-1,3-butadiene.

![Neoprene Synthesis](image)

In this illustration, the dashed lines represent repetition of the same base units, so both the products and reactants are polymers. The reaction proceeds with a mechanism similar to the Friedel-Crafts mechanism. Cross-linkage between the chlorine atom of one chain and the double bond of another contributes to the overall elasticity of neoprene. This cross-linkage occurs as the chains lie next to each other at random angles, and the attractions between double bonds prevent them from sliding back and forth.

**Colored molecules**

The conjugated double bonds in beta-carotene produce the orange color in carrots. The conjugated double bonds in lycopene produce the red color in tomatoes.

![β carotene](image)

![lycopene](image)

**Outside links**

Problem

Draw out the mechanism for the natural synthesis of rubber from 3-methyl-3-butenyl pyrophosphate and 2-methyl-1,3-butadiene. Show the movement of electrons with arrows.

Answer

![Mechanism for natural rubber synthesis](image)

Exercises

Questions

Q14.6.1

Draw a segment for the polymer that may be made from 2-tert-butyl-1,3-butadiene.

Q14.6.2

Propose the mechanism for the acid catalyzed polymerization of 2-methyl-1,3-butadiene.

Solutions

S14.6.1
The initial step is an addition of a hydrogen from the acid, followed by the polymerization.

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