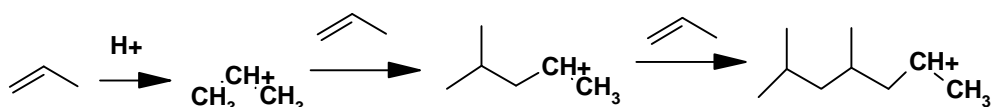


POLYMERS AND PLASTICS

The technical term "plastic" means "deforming irreversibly under tension or compression"; it is the opposite of "elastic", the term describing materials which spring back after compression or tension. Because so many man-made materials are plastic and thus can be molded, the term has been applied to the materials which technically are "polymers". Polymers consist of large molecules comprised of many (1000 to 100,000) identical covalently bonded units called monomers, combined by a process called polymerization. The polymer material is actually a complex mixture of molecules with the same repeating structure but different lengths; because they are mixtures, they have low "melting points". Most polymers do not crystallize: upon cooling, they become quite rigid and brittle, like glass at a fairly sharp temperature called the glass-transition temperature T_g (glass is *also* a thick liquid). If they are too rigid for the desired use, they are softened by addition of low molecular weight materials like dibutyl phthalate. Some polymers have crystalline regions, whose edges of reflect light and make the polymer cloudy.

ALKENE ADDITION POLYMERS

Alkenes can be converted to cations, radicals, anions and organometallic compounds (C-M bonds), each of which can add to another molecule of alkene to produce another reactive species which adds to the next alkene, etc. A simple example is propene, which can be converted into a growing polymer carbocation by acid (some CH_3 's and CH 's are shown explicitly to help improve clarity):

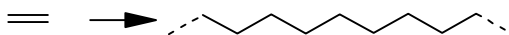


Alteration of the catalyst, temperature and pressure alters the chain length, and can encourage branching or cross-linking of neighboring chains (by hydrogen abstraction to generate a reactive site in mid-chain); as a result, a polymer like polyethylene can be generated with different properties depending on the reaction conditions (the most common are low density, LDPE. and high density, HDPE). Polypropylene has a series of chiral centers, discussed below.

Addition polymers are used for a variety of purposes:

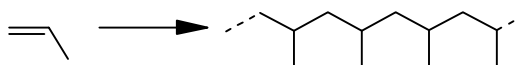
polyethylene

LDPE: bags, elec. insulation, squeeze bottles;
HDPE: bottle caps, pipes, TV cabinets



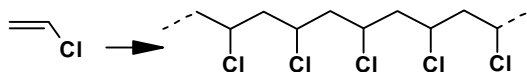
polypropylene

wear-resistant carpets, thermal underwear



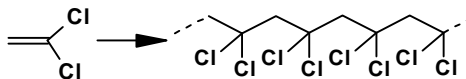
polyvinylchloride (PVC)

pipes, Naugahyde (TM), phono. records



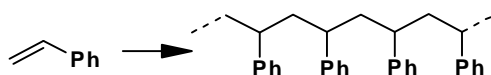
polyvinylidenechloride (Saran)

food wrap



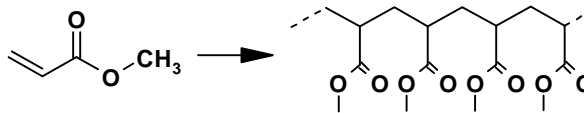
polystyrene (Ph = phenyl)

toys, styrofoam

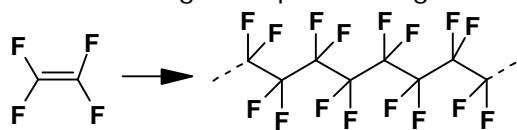


polymethyl methacrylate (lucite)

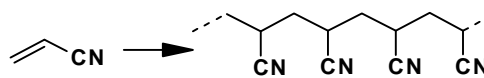
windows, bowling balls



polytetrafluoroethylene (PTFE, teflon)
bearings and pot coatings



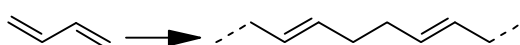
polyacrylonitrile (Orlon, Acrilan)
sweaters, wigs



DIENE ADDITION POLYMERS

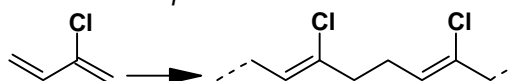
Addition to dienes occurs with a strong preference for 1,4 addition, just as is observed for additions of HCl or Br₂, with all catalysts. Synthetic examples include two rubber substitutes:

polybutadiene



and

chloroprene

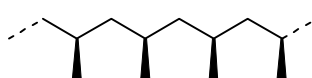


A wider variety of addition polymers are created by making polymers of two or more alkenes, copolymers rather than homopolymers. Random copolymerization of styrene (25%) and butadiene (75%) produces the most popular synthetic rubber, SBR (styrene-butadiene rubber).

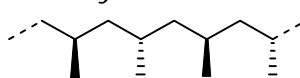
STEREOCHEMISTRY

Polypropylene has a series of chiral centers, one for each monomer unit. Although it is impossible to label these (*R*) or (*S*), the *anti* conformation clearly shows three diastereomers: *isotactic* (all CH₃ on same side), *syndiotactic* (CH₃ alternating) and *atactic* (random). Specialized catalysts are available to make each form (*atactic* is easy).

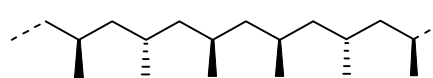
isotactic



syndiotactic

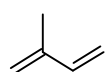


atactic

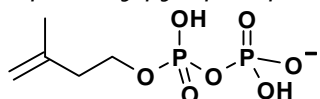


Natural rubber is an addition polymer, made from a phosphate ester of isoprene (2-methyl-1,3-butadiene). The double bond in the polyisoprene is generated by the rubber tree stereospecifically (*Z*) or *cis*. Man-made polyisoprene is predominantly the more stable (*E*) or *trans*.

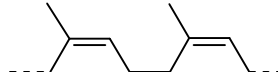
isoprene



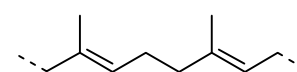
isopentenylpyrophosphate



natural (*Z*)-polyisoprene



(*E*)-polyisoprene



Natural rubber is useless as removed from the tree - latex is a sap, after all. Goodyear discovered that sulfur reacted with hot rubber and made it stiff, a process he called vulcanization. The sulfur reacts with some of the remaining double bonds to cross-link adjacent chains; alas, crosslinking the (*E*) isomer does not produce a rubber substitute but a sticky mess.

FURTHER READING

- L. Mandelkern, *An Introduction to Macromolecules*, Springer Verlag, NY 1972, 1983.
 K. F. O'Driscoll, *The Nature and Chemistry of High Polymers*, Reinhold, NY, 1964.
 R. B. Seymour, C. E. Carraher, Jr. *Polymer Chemistry: An Introduction*, M. Dekker, NY, 1981.

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