doi:10.1351/goldbook.C00958

chain polymerization

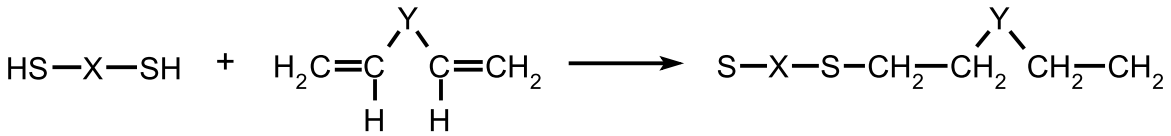
Also contains definition of: condensative chain polymerization

A chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s) and reactive site(s) on the polymer chain with regeneration of the reactive site(s) at the end of each growth step.
Notes:

1. A chain polymerization consists of initiation and propagation reactions, and may also include termination and chain transfer reactions.
2. The adjective 'chain' in 'chain polymerization' denotes a 'chain reaction' rather than a 'polymer chain'.
3. Propagation in chain polymerization usually occurs without the formation of small molecules. However, cases exist where a low-molar-mass by-product is formed, as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed amino-acid *N*-carboxy anhydrides). When a low-molar-mass by-product is formed, the adjective 'condensative' is recommended to give the term condensative chain polymerization
4. The growth steps are expressed by:

   $$P_x + M \rightarrow P_{x+1}\ (+L) \qquad \{x\} \in \{1, 2, ...\infty\}$$

   where P_x denotes the growing chain of degree of polymerization x, M a monomer and L a low-molar-mass by-product formed in the case of condensative chain polymerization.
5. The term 'chain polymerization' may be qualified further, if necessary, to specify the type of chemical reactions involved in the growth step, e.g. ring-opening chain polymerization, cationic chain polymerization.
6. There exist, exceptionally, some polymerizations that proceed *via* chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization:

   proceeds *via* a radical chain reaction with intermolecular transfer of the radical centre. The growth step, however, involves reactions between molecules of all degrees of polymerization and, hence, the polymerization is classified as a polyaddition. If required, the classification can be made more precise and the polymerization described as a chain-reaction polyaddition.

doi:10.1351/goldbook.C00958

Source:
PAC, 1996, *68*, 2287 *(Glossary of basic terms in polymer science (IUPAC Recommendations 1996))* on page 2306

