

*A one-stop, at-your-fingertips source of information for students, researchers, technologists, and industrial managers, this book as a single reference of the conventional and controlled/living radical polymerization methods.*

Can two polymer chains be the same length? They can if you use living polymerization. As defined by the International Union of Pure and Applied Chemistry IUPAC definition, living polymerization is a chain polymerization from which chain transfer and chain termination are absent. Living polymerization is used to produce materials with narrow molecular weight distribution, an important property for many polymer applications.

**Polymerization Process** There are four general processes occurring simultaneously during the polymerization process: In simple terms, each polymer chain starts to grow, propagates, and terminates at a certain time, and synchronizing these processes results in chains of similar length, or molecular weight, which is desirable. If the chain initiation rate is slower or comparable to propagation rate, some chains are being initiated while others are rapidly growing, resulting in longer and shorter chains. On the other hand, if initiation is much faster than the propagation, polymer chains start growing simultaneously, and grow uniformly. Now, if the chains are not terminated by any additional mechanism, the only factor defining their growth is the presence of a monomer. Once the monomer is depleted, the growth is complete, with resulting polymer chains of the same length. Living polymerization, which has been studied for more than 70 years, can follow anionic, cationic, and radical polymerization mechanisms. Popular atom transfer radical polymerization ATRP and reversible addition-fragmentation chain transfer RAFT are examples of living radical polymerization. Living polymerization allows you to obtain precisely controlled molecular weight and narrow molecular weight distribution, as well as complex polymer architectures.

**Practical Applications** One of the exciting practical applications of living polymerization is nucleic acid-based therapeutics or gene therapy, which is being actively studied to treat hereditary and infectious diseases. Polymers are used for nanoparticle delivery of nucleic acids inside the cell. An article in *Accounts of Chemical Research* explains: Because of their self-assembly with nucleic acids into virus-sized nanoparticles and high transfection efficiency in vitro, cationic polymers have been extensively studied for nucleic acid delivery applications, but toxicity and particle stability have limited the clinical applications of these systems. The advent of living free radical polymerization has improved the quality, control, and reproducibility of these synthesized materials. This process yields well-defined, narrowly dispersed materials with designed architectures and molecular weights. As a result, researchers can study the effects of polymer architecture and molecular weight on transfection efficiency and cytotoxicity.

**Supramolecular Design** The idea of living polymerization has been taken one step further by scientists from National Institute for Materials Science Japan, whose recent publication in *Nature Chemistry* describes the first application of living polymerization to the supramolecular domain, which mimics nature in the ways it assembles macromolecular structures. The scientists designed and studied living supramolecular polymerization of the porphyrin-based monomers into nanoparticles and nanofibers: Despite the fact that the polymerization is non-covalent, the reaction kinetics are analogous to that of conventional chain growth polymerization, and the supramolecular polymers were synthesized with controlled length and narrow polydispersity. Dispersity formerly referred to as polydispersity index is a measure of the heterogeneity of sizes of molecules in a material. When applying rational design to polymers to obtain materials with desired properties, we always aim to obtain monodisperse uniform plastic materials, so that they can behave in a uniform, predicted fashion. Living polymerization, among other controlled polymerization techniques, is a good way to get there. Takeuchi, *Nature Chemistry* 6, doi: 10.1038/nchem.1411, *Accounts of Chemical Research*, July 17, 2013, ; 45 7: Pun, *Biomacromolecules*, January 14, 2014, ;14 1: Non Living Polymerization Animation, Wikipedia. Living Polymerization Animation, Wikipedia.

**Chapter 2 : Radical polymerization - Wikipedia**

*Free-radical polymerization (FRP) is a method of polymerization by which a polymer forms by the successive addition of free-radical building blocks. Free radicals can be formed by a number of different mechanisms, usually involving separate initiator molecules.*

Contributors All the monomers from which addition polymers are made are alkenes or functionally substituted alkenes. The most common and thermodynamically favored chemical transformations of alkenes are addition reactions. Many of these addition reactions are known to proceed in a stepwise fashion by way of reactive intermediates, and this is the mechanism followed by most polymerizations. A general diagram illustrating this assembly of linear macromolecules, which supports the name chain growth polymers, is presented here. Indeed, cases of explosively uncontrolled polymerizations have been reported. It is useful to distinguish four polymerization procedures fitting this general description. Radical Chain-Growth Polymerization Virtually all of the monomers described above are subject to radical polymerization. Since this can be initiated by traces of oxygen or other minor impurities, pure samples of these compounds are often "stabilized" by small amounts of radical inhibitors to avoid unwanted reaction. When radical polymerization is desired, it must be started by using a radical initiator, such as a peroxide or certain azo compounds. The formulas of some common initiators, and equations showing the formation of radical species from these initiators are presented below. By using small amounts of initiators, a wide variety of monomers can be polymerized. One example of this radical polymerization is the conversion of styrene to polystyrene, shown in the following diagram. The first two equations illustrate the initiation process, and the last two equations are examples of chain propagation. Each monomer unit adds to the growing chain in a manner that generates the most stable radical. Since carbon radicals are stabilized by substituents of many kinds, the preference for head-to-tail regioselectivity in most addition polymerizations is understandable. Because radicals are tolerant of many functional groups and solvents including water, radical polymerizations are widely used in the chemical industry. In principle, once started a radical polymerization might be expected to continue unchecked, producing a few extremely long chain polymers. In practice, larger numbers of moderately sized chains are formed, indicating that chain-terminating reactions must be taking place. The most common termination processes are Radical Combination and Disproportionation. These reactions are illustrated by the following equations. The growing polymer chains are colored blue and red, and the hydrogen atom transferred in disproportionation is colored green. Note that in both types of termination two reactive radical sites are removed by simultaneous conversion to stable products. Since the concentration of radical species in a polymerization reaction is small relative to other reactants. The relative importance of these terminations varies with the nature of the monomer undergoing polymerization. For acrylonitrile and styrene combination is the major process. However, methyl methacrylate and vinyl acetate are terminated chiefly by disproportionation. Another reaction that diverts radical chain-growth polymerizations from producing linear macromolecules is called chain transfer. As the name implies, this reaction moves a carbon radical from one location to another by an intermolecular or intramolecular hydrogen atom transfer colored green. These possibilities are demonstrated by the following equations Chain transfer reactions are especially prevalent in the high pressure radical polymerization of ethylene, which is the method used to make LDPE low density polyethylene. Further polymerization at the new radical site generates a side chain radical, and this may in turn lead to creation of other side chains by chain transfer reactions. As a result, the morphology of LDPE is an amorphous network of highly branched macromolecules.

**Chapter 3 : Living Polymerization and Molecular Weight |**

*Handbook of Radical Polymerization provides a concise source of information on mechanisms, synthetic techniques, and characterization methods and addresses future trends for polymers made by free radical intermediates.*

We would like to dedicate this article to P. Plesch, a pioneer of cationic polymerization and a mentor and friend for many of those who are now at the forefront of this field of science. He passed away 5 March at the age of 78. We will miss him. This short, introductory review covers the still rapidly growing and industrially important field of ring opening polymerization ROP. Nevertheless, the different groups of cyclic monomers are considered olefins, ethers, thioethers, amines, lactones, thiolactones, lactams, disulfides, anhydrides, carbonates, silicones, phosphazenes and phosphonites and the mechanisms by which they can be polymerized involving a ring-opening polymerization. Literature up to 2000 has been considered but the citations selected refer to detailed reviews and key papers, describing not only the latest developments but also the evolution of the current state of the art. Introduction Ring-opening polymerization ROP is, together with chain radical and ionic polymerization and condensation polymerization, one of the three paths to the polymers that are so important to life in the 21st century. Some ROP can be considered as a chain polymerization addition of monomer to a growing chain end but many reactions are more complicated and involve, e. Particularly ROP has proved to be a useful synthetic route to technologically interesting polymers with very specific, and controllable properties e. Since this review is intended more as an introduction to the field of ROP, no attempt will be made to describe the particularities of the thermodynamics of these polymerizations. It should however be noted that rather than the driving force for the polymerization being the conversion of a multiple to a single bond, for most ROP the driving force is the ring strain and associated steric considerations. Additionally, there is the consideration of the ring chain equilibrium, which leads to the considerable influence of the initial monomer concentration and temperature on the microstructure of the products. The interested reader is referred to the excellent recent summary by Duda and Kowalski [ 1 ]. Additionally, ROP is not aided by the enthalpy difference between a single and double C=C bond, which counteracts the loss of entropy occurring as a consequence of polymerization via chain polymerization. ROP have in common that the monomers are rings, irrespective of ring size, but the reason why polymerization takes place can vary. Rings composed of 3-8 atoms may polymerize due to the loss of enthalpy associated with the loss of ring strain. Strain-free six-membered rings do not generally polymerize. For rings containing disulfide, silicon or carbonate moieties an additional effect is the increased rotational freedom of these groups in the resulting linear chains which leads to an increase in entropy to give the driving force for polymerization [ 4 ]. Many polymers of industrial importance are produced via ROP, e. A large family of commercially available polymers called polyethylenimines many of which are highly branched, are produced via a CROP of aziridine or oxazoline monomers. Polyoxymethylene POM, derived from trioxane and most of the diols produced, e. More recently, polyglycolides and polylactides see Section 4. Another important development is the use of metathesis catalysts to open rings with exo functional groups to yield novel polymer structures Section 5. Table 1 lists the major groups of ring structures and the mechanism by which they are usually polymerized. This review is organized according to mechanism rather than molecular types and is designed to demonstrate the usefulness of this type of polymerization to yield novel polymers, particularly for those new to the subject. It is hoped that it will provide a useful start for entering the field rather than being an exhaustive review of all the literature to date. It is recommended that the interested reader refer to, e. Typical cyclic monomers and their usual polymerization mechanism [ 4 ].

*(Co)polymers prepared via free radical mechanism, together with polyolefins, comprise the largest portion of the commodity plastics industry and are also used for preparation of many specialty materials. Handbook of Radical Polymerization provides a concise source of information on mechanisms.*

Reaction of polymer chain R with other species in reaction Propagation[ edit ] During polymerization, a polymer spends most of its time in increasing its chain length, or propagating. After the radical initiator is formed, it attacks a monomer Figure The other is more loosely held in a pi bond. The free radical uses one electron from the pi bond to form a more stable bond with the carbon atom. The other electron returns to the second carbon atom, turning the whole molecule into another radical. This begins the polymer chain. Figure 12 shows how the orbitals of an ethylene monomer interact with a radical initiator. Phenyl initiator from benzoyl peroxide BPO attacks a styrene molecule to start the polymer chain. An orbital drawing of the initiator attack on ethylene molecule, producing the start of the polyethylene chain. Once a chain has been initiated, the chain propagates Figure 13 until there are no more monomers living polymerization or until termination occurs. There may be anywhere from a few to thousands of propagation steps depending on several factors such as radical and chain reactivity, the solvent, and temperature. Propagation of polystyrene with a phenyl radical initiator. Termination[ edit ] Chain termination will occur unless the reaction is completely free of contaminants. In this case, the polymerization is considered to be a living polymerization because propagation can continue if more monomer is added to the reaction. Living polymerizations are most common in ionic polymerization, however, due to the high reactivity of radicals. Termination can occur by several different mechanisms. If longer chains are desired, the initiator concentration should be kept low; otherwise, many shorter chains will result. One can determine if this mode of termination is occurring by monitoring the molecular weight of the propagating species: Also, combination will result in a polymer that is C<sub>2</sub> symmetric about the point of the combination. Termination by the combination of two poly vinyl chloride PVC polymers. Termination by disproportionation of poly methyl methacrylate. Combination of an active chain end with an initiator radical Figure Termination of PVC by reaction with radical initiator. Interaction with impurities or inhibitors. Oxygen is the common inhibitor. The growing chain will react with molecular oxygen, producing an oxygen radical, which is much less reactive Figure This significantly slows down the rate of propagation. Inhibition of polystyrene propagation due to reaction of polymer with molecular oxygen. Nitrobenzene , butylated hydroxyl toluene, and diphenyl picryl hydrazyl DPPH , Figure 18 are a few other inhibitors. The latter is an especially effective inhibitor because of the resonance stabilization of the radical. Chain transfer[ edit ] Contrary to the other modes of termination, chain transfer results in the destruction of only one radical, but also the creation of another radical. Often, however, this newly created radical is not capable of further propagation. Similar to disproportionation , all chain transfer mechanisms also involve the abstraction of a hydrogen or other atom. There are several types of chain transfer mechanisms. Chain transfer from polystyrene to solvent. The effectiveness of chain transfer involving solvent molecules depends on the amount of solvent present more solvent leads to greater probability of transfer , the strength of the bond involved in the abstraction step weaker bond leads to greater probability of transfer , and the stability of the solvent radical that is formed greater stability leads to greater probability of transfer. Halogens , except fluorine , are easily transferred. While this does create a radical on the affected monomer, resonance stabilization of this radical discourages further propagation Figure Chain transfer from polypropylene to monomer. This initiator can then begin new polymer chains. Therefore, contrary to the other forms of chain transfer, chain transfer to the initiator does allow for further propagation. Peroxide initiators are especially sensitive to chain transfer. Chain transfer from polypropylene to di-t-butyl peroxide initiator. This terminates the growth of one polymer chain, but allows the other to branch and resume growing. This reaction step changes neither the number of polymer chains nor the number of monomers which have been polymerized, so that the number-average degree of polymerization is unaffected. Chain transfer from polypropylene to backbone of another polypropylene. Effects of chain transfer: The most obvious effect of chain transfer is a

decrease in the polymer chain length. If the rate of transfer is much larger than the rate of propagation, then very small polymers are formed with chain lengths of repeating units telomerization.

### Chapter 5 : Braslau Group: $\hat{\pm}$ -H Nitroxides in NMP

*One example of this radical polymerization is the conversion of styrene to polystyrene, shown in the following diagram. The first two equations illustrate the initiation process, and the last two equations are examples of chain propagation.*

### Chapter 6 : Atom transfer radical polymerization - Wikipedia

*Ring-opening polymerization (ROP) is, together with chain (radical and ionic) polymerization and condensation polymerization, one of the three paths to the polymers that are so important to life in the.*

### Chapter 7 : Handbook of Radical Polymerization, Cat# $\hat{\ll}$ racedaydvl.com

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### Chapter 8 : Books and Book Chapters - Matyjaszewski Polymer Group - Carnegie Mellon University

*Vol. 11 RADICAL POLYMERIZATION Scheme 2. accompanied by so-called vinyl polymerization without ring opening of the cyclic structure. Although fewer monomers undergo RROP than cationic, anionic, and coor-.*

### Chapter 9 : Free Radical Polymerization - Chemistry LibreTexts

*In this work, we continue our investigations of the application of choline salts as activators in free-radical polymerization of itaconic acid. We focused on aqueous solutions of the salts and propose possible explanation of the acceleration effect on the rate of the polymerization.*