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There are a number of methods used to synthetically prepare biopolymers, their models, and bioanalogous polymers. This work approaches the syntheses of the three major groups of biopolymers existing in nature - polypeptides, polysaccharides, and nucleic and teichoic acids - by ring-opening polymerization.

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2: Models of Biopolymers By Ring-Opening Polymerization - CRC Press Book

Summary There are a number of methods used to synthetically prepare biopolymers, their models, and bioanalogous polymers. This work approaches the syntheses of the three major groups of biopolymers existing in nature - polypeptides, polysaccharides, and nucleic and teichoic acids - by ring-opening polymerization.

History[edit] Ring-opening polymerization ROP has been used since the beginning of the s in order to synthesize polymers. Synthesis of polypeptides which has the oldest history of ROP, dates back to the work in by Leuchs. Mechanisms and thermodynamics of ring-opening polymerization was further established in the s. ROP can introduce functional groups such as ether , ester , amide , and carbonate into the polymer main chain, which cannot be achieved by vinyl polymerization affording polymers only with C-C main chain. Polymers obtained by ROP can be also prepared by polycondensation in most cases, but following controlled radical polymerization is possible in ROP, which is difficult in polycondensation. Recently, development of novel monomers and catalysts has enabled polymer chemists to control molecular weights , structure, and configuration of the polymers precisely. When the reactive center of the propagating chain is a carbocation , the polymerization is called cationic ring-opening polymerization. Mechanisms[edit] Ring-opening polymerization can proceed via radical , anionic or cationic polymerization as described below in more details. ROP can involve metal catalysts too and is best exemplified by the polymerization of olefins while maintaining unsaturation in the resulting polymer. This mechanism is known as ring-opening metathesis polymerization ROMP. Radical ring-opening polymerization[edit] Main article: Radical polymerization With radical ring-opening polymerization, it is possible to produce polymers of the same or lower density than the monomers. This is important for applications that require constant volume after polymerization, such as tooth fillings , coatings, and the molding of electrical and electronic components. For instance, radical ROP can produce polymers with ethers , esters , amides , and carbonates as functional groups along the main chain. Degradable polyester can be synthesized via radical ring-opening homo- and copolymerization. The goal is to synthesize a final copolymer that is both hydrolyzable and photodegradable. There are two typical mechanistic schemes in radical ROP. The terminal vinyl group accepts a radical. The radical will be transformed into a carbon radical stabilized by functional groups i. This will lead to the generation of an internal olefin. Radical ring-opening polymerization of vinyl cyclopropane Scheme 2: In this case, the exo-methylene group is the radical acceptor. The ring-opening reaction will form an ester bond, and the radical produced is stabilized by a phenyl group. Anionic ring-opening polymerization[edit] Main article: Anionic polymerization The general mechanism for anionic ring-opening polymerization. Polarized functional group is represented by X-Y, where the atom X usually a carbon atom becomes electron deficient due to the highly electron-withdrawing nature of Y usually an oxygen, nitrogen, sulfur, etc. The nucleophile will attack atom X, thus releasing Y-. The newly formed nucleophile will then attack the atom X in another monomer molecule, and the sequence would repeat until the polymer is formed. Monomers with a three-member ring structure - such as epoxide , aziridine , and episulfide - are able to undergo anionic ROP due to the ring-distortion, despite having a less electrophilic functional group e. These cyclic monomers are important for many practical applications. The polarized functional group in cyclic monomers is characterized by one atom usually a carbon that is electron-deficient due to an adjacent atom that is highly electron-withdrawing e. Ring-opening will be triggered by the nucleophilic attack of the initiator to the carbon, forming a new species that will act as a nucleophile. The sequence will repeat until the polymer is formed. The monomers that undergo AROP will contain polarized bonds ester carbonate , amide , urethane , and phosphate , which respectively leads to the production of the corresponding polyester , polycarbonate , polyamide , polyurethane and polyphosphate. Another possible mechanism for propagation is the nucleophilic attack of an activated monomer to the growing chain end. The active centers of AROP monomers are nucleophilic and also act as bases to abstract protons from the monomer, initiating new chains. Thus, AROP often results in low molecular-weight polymers. A possible method to increase the molecular mass of the polymer products is by adding crown ethers as complexing agents for counter-ions in the polymerization system. This causes the free-ions to preferentially add to

monomer rather than abstract protons. Cationic ring-opening polymerization CROP is characterized by having a cationic initiator and intermediate. Examples of cyclic monomers that polymerize through this mechanism include lactones, lactams, amines, and ethers. For example, if the atom bearing the positive charge is stabilized by electron-donating groups, polymerization will proceed by the SN1 mechanism. Not all cyclic monomers containing an heteroatom undergo CROP. Ring size influences whether the cyclic monomer polymerize through this mechanism. For example, 4, 6 and 7-membered rings of cyclic esters polymerize through CROP. Therefore, cyclic monomers with small or lacking ring strain will not polymerize. Propagation[edit] The cationic species is an heteroatom and the chain grows by the addition of cyclic monomers thereby opening the ring system. In CROP, three mechanisms are distinguished by the propagating species. This mechanism is observed when the monomer is in low concentration. When it is a tertiary ion, polymerization proceeds by linear growth. The monomer can likewise be activated i. Termination[edit] CROP can be considered as a living polymerization and can be terminated by intentionally adding termination reagents such as phenoxy anions, phosphines or polyanions. The active end can "backbite" the chain, forming a macrocycle. Alkyl chain transfer is also possible, where the active end is quenched by transferring an alkyl chain to another polymer. Ring-opening metathesis polymerization[edit] Main article: Ring-opening metathesis polymerization Ring opening metathesis polymerization of olefin. Ring-opening metathesis polymerization ROMP is used for making unsaturated polymers from olefin monomers that are typically cycloalkenes or bicycloalkenes. It involves organometallic catalysts of transition metals such as W, Mo, Re, Ru, and Ti carbenes complexes. The enthalpy for relieving the ring strain must be very favorable for ROMP to occur because the entropy decreases during polymerization see Gibbs free energy. Cyclic alkenes of 5, 7, and 8 member rings, for example, undergo ROMP at room temperature, whereas the 6 member ring analog does not. The growing chain can be terminated by adding an alkene, usually ethyl vinyl ether, to remove the polymer from the metal catalyst. Some commercially relevant unsaturated polymers are synthesized by ROMP, such as Norsorex polynorbornene, Vestenamer polycyclooctene, and Metton polycyclopentadiene. Catalysts for ROMP[edit].

3: Amazon | Models of Biopolymers By Ring-Opening Polymerization | Stanislaw Penczek | Organic

MODELS OF BIOPOLYMERS BY RINGOPENING POLYMERIZATION OF CYCLIC PHOSPHORUS CONTAINING COMPOUNDS S. Penczek Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Ćdi, Boczna 5, Poland Abstract - Methods are described, allowing the preparation of the high molecular weight polyesters of phosphoric acid, with a sequence of atoms in the main chain similar to that in.

4: Zubal Books Complete Catalog Page

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5: Ring-opening polymerization - Wikipedia

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6: METHOXIDE - Definition und Synonyme von methoxide im Wörterbuch Englisch

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