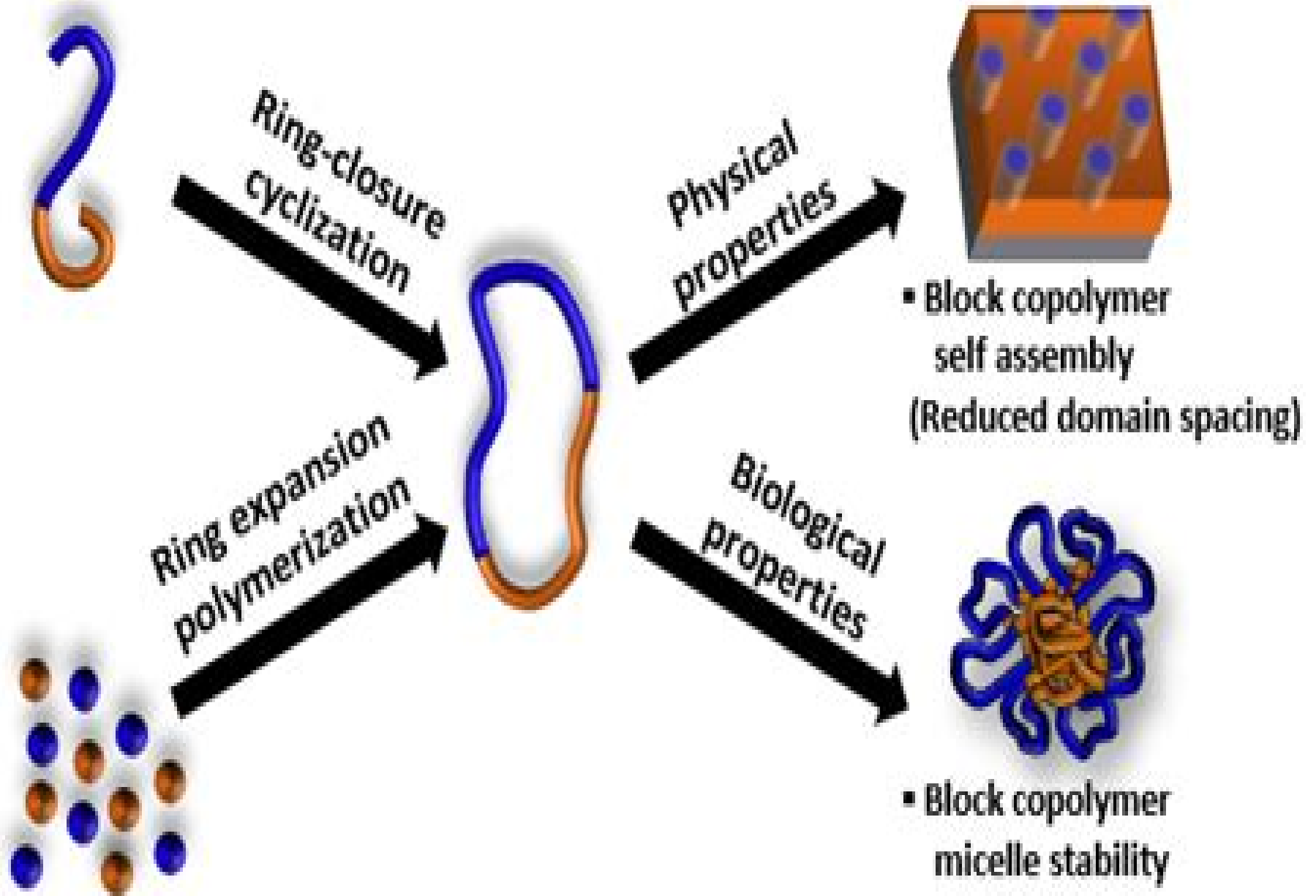


Advanced synthetic strategies

New applications



Cyclic Polymers

E.R. Semlyen



Cyclic Polymers:

Cyclic Polymers E.R. Semlyen, 2007-05-08 *Cyclic Polymers* Second Edition reviews the many recent advances in this rapidly expanding subject since the publication of the first edition in 1986. The preparation, characterisation, properties and applications of a wide range of organic and inorganic cyclic oligomers and polymers are described in detail together with many examples of catenanes and rotaxanes. The importance of large cyclics in biological chemistry and molecular biology is emphasised by a wide coverage of circular DNA, cyclic peptides and cyclic oligosaccharides and polysaccharides. Experimental techniques and theoretical aspects of cyclic polymers are included as well as examples of their uses such as ring opening polymerisation reactions to give commercially important materials. This book covers a wide range of topics which should be of interest to many scientific research workers for example in polymer science, chemistry and molecular biology as well as providing a reference text for undergraduate and graduate students. *Cyclic Polymers* E.R.

Semlyen, 2012-12-06 Synthetic polymers based on long chain molecules have been investigated intensively for over 50 years. They have found important applications as plastics, fibres, rubbers and other materials. The chain molecules may be simple linear structures or they may be branched or cross linked. During the past decade, sharp fractions of the first synthetic cyclic polymer have been prepared. These fractions of cyclic polydimethyl siloxane consist of ring molecules containing hundreds of skeletal bonds. Some of their properties have been found to be quite different from those of the corresponding linear polymers. Synthetic cyclic polymers including cyclic polystyrene have joined the naturally occurring circular DNAs as examples of substantially large ring molecules. This book aims to review current knowledge of cyclic polymers and biological ring macromolecules. In addition, it discusses theories of cyclic macromolecules and describes cyclization processes involving long chain molecules. Since 1865 when Kekulé proposed a simple ring structure for benzene, larger and larger ring molecules have been synthesized in the laboratory and discovered in nature. Many more examples are to be expected in the future. In time, large ring molecules should take their proper place alongside long chain molecules as one of the two possible constituent structural units of polymers. **Topological Polymer Chemistry: Progress Of Cyclic Polymer In Syntheses, Properties And Functions** Yasuyuki Tezuka, 2012-12-17

There are examples aplenty in the macroscopic world that demonstrate the form of objects directing their functions and properties. On the other hand, the fabrication of extremely small objects having precisely defined structures has only recently become an attractive challenge which is now opening the door to nanoscience and nanotechnology. In the field of synthetic polymer chemistry, a number of critical breakthroughs have been achieved during the first decade of this century to produce an important class of polymers having a variety of cyclic and multicyclic topologies. These developments now offer unique opportunities in polymer materials design to create unprecedented properties and functions simply based on the form i.e. topology of polymer molecules. In this book on topological polymer chemistry, the important developments in this growing area will be collected for the first time with

particular emphasis on new conceptual insights for polymer chemistry and polymer materials The book will systematically review topological polymer chemistry from basic aspects to practice and give a broad overview of cyclic polymers covering new synthesis structure characterization basic properties functions and the eventual applications Cyclic Polymers E. R. Semlyen, 2014-01-15

Topological Polymer Chemistry Yasuyuki Tezuka, Tetsuo Deguchi, 2022-02-25 This book provides a comprehensive description of topological polymers an emerging research area in polymer science and polymer materials engineering The precision polymer topology designing is critical to realizing the unique polymer properties and functions leading to their eventual applications The prominent contributors are led by Principal Editor Yasuyuki Tezuka and Co Editor Tetsuo Deguchi Important ongoing achievements and anticipated breakthroughs in topological polymers are presented with an emphasis on the spectacular diversification of polymer constructions The book serves readers collectively to acquire comprehensive insights over exciting innovations ongoing in topological polymer chemistry encompassing topological geometry analysis classification physical characterization by simulation and the eventual chemical syntheses with the supplementary focus on the polymer folding invoked with the ongoing breakthrough of the precision AI prediction of protein folding The current revolutionary developments in synthetic approaches specifically for single cyclic ring polymers and the topology directed properties functions uncovered thereby are outlined as a showcase example This book is especially beneficial to academic personnel in universities and to researchers working in relevant institutions and companies Although the level of the book is advanced it can serve as a good reference book for graduate students and postdocs as a source of valuable knowledge of cutting edge topics and progress in polymer chemistry

New Frontiers in Polymer Synthesis Shiro Kobayashi, 2008-09-26 It is generally accepted that a new material is often developed by finding a new synthesis method of reaction or a new reaction catalyst Historically a typical example may be referred to as a Ziegler Natta catalyst which has allowed large scale production of petroleum based polyolefins since the middle of the 20th century New polymer synthesis therefore will hopefully lead to creation of new polymer materials in the 21st century This special issue contributed by three groups focuses on recent advances in polymer synthesis methods which handle the cutting edge aspects of the advanced technology The first article by Yokozawa and coworkers contains an overview of the reaction control in various condensation polymerizations polycondensations Advanced technologies enabled the control of stereochemistry regiochemical and enantioselections chemoselectivity chain topology and stoichiometry of monomers giving a high molecular weight polymer It has been recognized for a long time however that polycondensation is a difficult process in controlling the reaction pathway because the reaction is of step growth and the reactivity of monomers oligomers and polymers are almost the same during the reaction and hence the molecular weight of polymers and its distribution M_w/M_n are impossible to regulate The authors group developed with a new reaction system chain growth condensation polymerization changing the nature of polycondensation from step growth to chain growth namely the propagating chain end is active allowing for control of the

product molecular weight as well as the distribution

Zwitterionic Polymerization for the Synthesis of High Molecular Weight Cyclic Polymers

Hayley A. Brown, 2013

Topological isomerism in macromolecules represents a fascinating field of study. Linear polymers form the basis of much of the current scientific understanding of bulk polymer behavior due to their simple structure and synthetic accessibility. In contrast, cyclic polymers remain poorly understood due to the difficulty in generating sufficient quantities of pure samples. In particular, high molecular weight samples where phenomena related to entanglement could be observed have eluded polymer chemists until recently. Among the several strategies employed for the synthesis of high molecular weight cyclic polymers, recent reports have highlighted the utility of zwitterionic ring opening polymerization (ZROP). Efforts to understand the N-heterocyclic carbene (NHC) mediated ring opening of strained lactones have led to the development of several mechanistic models. Kinetic studies on the NHC mediated polymerization of epsilon-caprolactone (CL) and delta-valerolactone (VL) were conducted to account for the notably high molecular weight cyclic polymers generated. While the two monomer systems are closely related and polymerize with the same NHC initiators, a difference in the dependence of the reaction rate on monomer is observed. A general mechanism is proposed for the polymerization of VL. Exploiting the utility of ZROP to generate high molecular weight poly-epsilon-caprolactone allowed for a comparative study on the bulk crystallization of cyclic PCL and linear PCL across a range of molecular weights. WAXS and SAXS studies show that linear and cyclic PCL exhibit the same global and local crystalline structure, but that cyclic PCL crystallizes more rapidly than linear PCL. Isothermal DSC crystallization kinetic studies support this observation and indicate that the difference in crystallization rate increases with increasing molecular weight. Approximating the equilibrium melting temperature of these samples using the Hoffmann-Weeks method indicates that there is no significant difference in T_m^0 between cyclic and linear PCL. In an attempt to broaden the scope of initiators for the ZROP of strained lactones, the use of amidines for the polymerization of lactide was explored. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were shown to mediate the ZROP of lactide to give predominantly cyclic poly(lactide) (PLA). A notable solvent effect was observed, with no polymerization occurring in neat tetrahydrofuran (THF), fast polymerization with formation of significant amounts of linear PLA in dichloromethane (DCM), and moderate rate of polymerization with minimal formation of linear PLA in THF/DCM blends. DFT computations suggest that the formation of a neutral tricyclic species, a zwitterionic species, and a ketene aminal are energetically feasible. This ketene aminal is thought to be the source of the linear PLA observed. Our efforts to develop a more hydrolytically stable family of cyclic polymers led to the investigation of the ZROP of strained cyclic carbosiloxanes. NHC mediated polymerization of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane occurs rapidly to give polymers with molecular weights exceeding 106 g/mol. While these polymerizations are difficult to control, the cyclic topology of the resulting polymers could be confirmed by comparative dilute solution viscosity studies and MALDI-TOF MS. As a complementary strategy to the use of neutral nucleophiles to initiate anionic-like

zwitterionic polymerization neutral Lewis acids were tested for the electrophilic zwitterionic ring opening polymerization EZROP of strained heterocycles Polymerization of 2 ethyl 2 oxaline proceeds slowly at elevated temperature with boron based Lewis acids to give HF capped linear chains determined by MALDI TOF MS In contrast the polymerization of 3,3-dimethyloxetane proceeds very rapidly at room temperature with B(C₆F₅)₃ to give a mixture of polymer products likely resulting from methyl scrambling between chains

N-heterocyclic Carbene Mediated Zwitterionic Polymerization for Cyclic Polymers Eun Ji Shin, 2011 Zwitterionic polymerization involves a propagating species with both positively and negatively charged groups Previous investigations on zwitterionic polymerization concern alternating copolymerization of nucleophilic and electrophilic monomers and polymerization of isolated stable zwitterionic monomers More recently the ring opening polymerization of cyclic monomers using nucleophilic initiators have been studied Specifically the zwitterionic polymerization of cyclic esters using N heterocyclic carbenes NHCs is the focus of this thesis The N heterocyclic carbene mediated zwitterionic polymerization of cyclic monomers provides an expedient route to polymers of various architectures such as cyclic polymers cyclic gradient copolymers and linear telechelic polymers The ring opening polymerization of lactide initiated by NHCs generates cyclic poly lactide s of defined molecular weight and molecular weight distribution Kinetic studies implicate a mechanism that involves a slow initiation step and a propagation step that is much faster than depropagation and chain termination by cyclization Stochastic simulations and chain extension experiments showed that only a fraction of the NHC forms the active zwitterion in solution leading to both chain extension of the zwitterions and re initiation of the NHC upon addition of the second batch of monomer These results prompted investigation of a more efficient way to prepare cyclic block copolymers The difference in reactivity of NHCs towards different monomers was exploited to synthesize cyclic block copolymers of valerolactone VL and caprolactone CL The faster ring opening of VL relative to CL resulted in a gradient cyclic copolymer comprised of VL rich sequences that transition to CL rich sequences in a cyclic macromolecule instead of a cyclic diblock copolymer This work not only provides a simple batch copolymerization protocol to produce cyclic gradient copolymers but also demonstrates the marked difference in reactivity of the NHCs compared to metal catalysts which produce random copolymers Stereocomplexation behavior has been observed in blends of linear poly L lactide and linear poly D lactide The influence of topology on the formation of stereocomplex was investigated using blends of linear and cyclic poly lactide s prepared by NHC mediated zwitterionic polymerization The linear cyclic and cyclic cyclic blends all form stereocomplexes when annealed Analyses of data from various characterization techniques indicate that the cyclic topology imposes constraints on the stereocomplexation formation The purity of the cyclic polymers is always a concern in the synthesis and physical property studies Attempts to identify and quantify the linear contamination in cyclic poly caprolactone samples are described Esterification reactions targeting the hydroxyl endgroups of linear contaminants were not successful but the macroinitiator approach where the linear contaminant in a cyclic polymer sample is used as the

macroinitiator to grow polymers to identify and remove the linear contamination shows promise A cyclic polymer more robust to post polymerization chemistry may be needed for more thorough purity studies **Hydrogeochemistry** ,1973
High Polymers ,1963 **Polymers for Biomedical Applications** Anil Mahapatro,Ankur S. Kulshrestha,2008-04-17
Research on applications of polymers for biomedical applications has increased dramatically to find improved medical plastics for this rapidly evolving field This book brings together various aspects of recent research and developments within academia and industry related to polymers for biomedical applications The Pyrolysis of Carbon Compounds Charles Dewitt Hurd,1929 *Government Reports Announcements & Index* ,1988 **Quarterly Reviews** Chemical Society (Great Britain),1947 *Journal American Chemical Society*,2003 **The Methylation of Para-aminophenol by Means of Formaldehyde** Ernest Carl Wagner,1921 *The Poet as Philosopher* Douglas Waples,Ernest Carl Wagner,Mabel Dodge Holmes,Melvin Gillison Rigg,Percy Van Dyke Shelly,Sadie Tanner Mossell,1921 **Polymer Preprints, Japan** ,2003
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