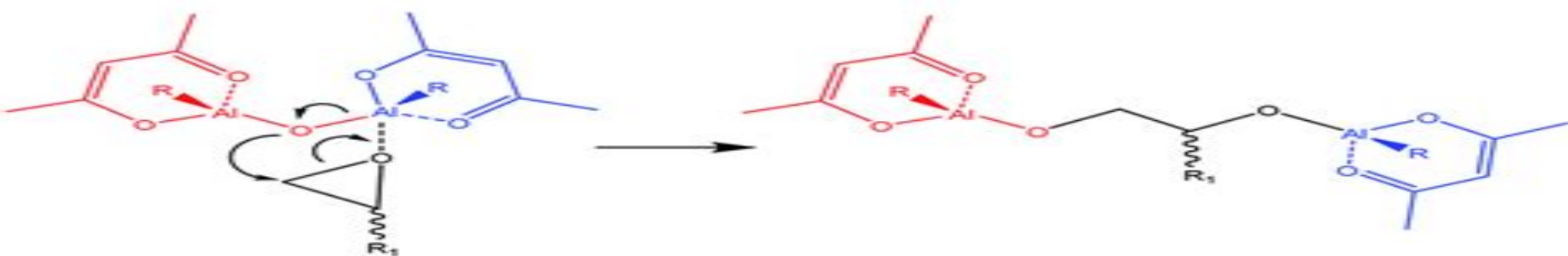
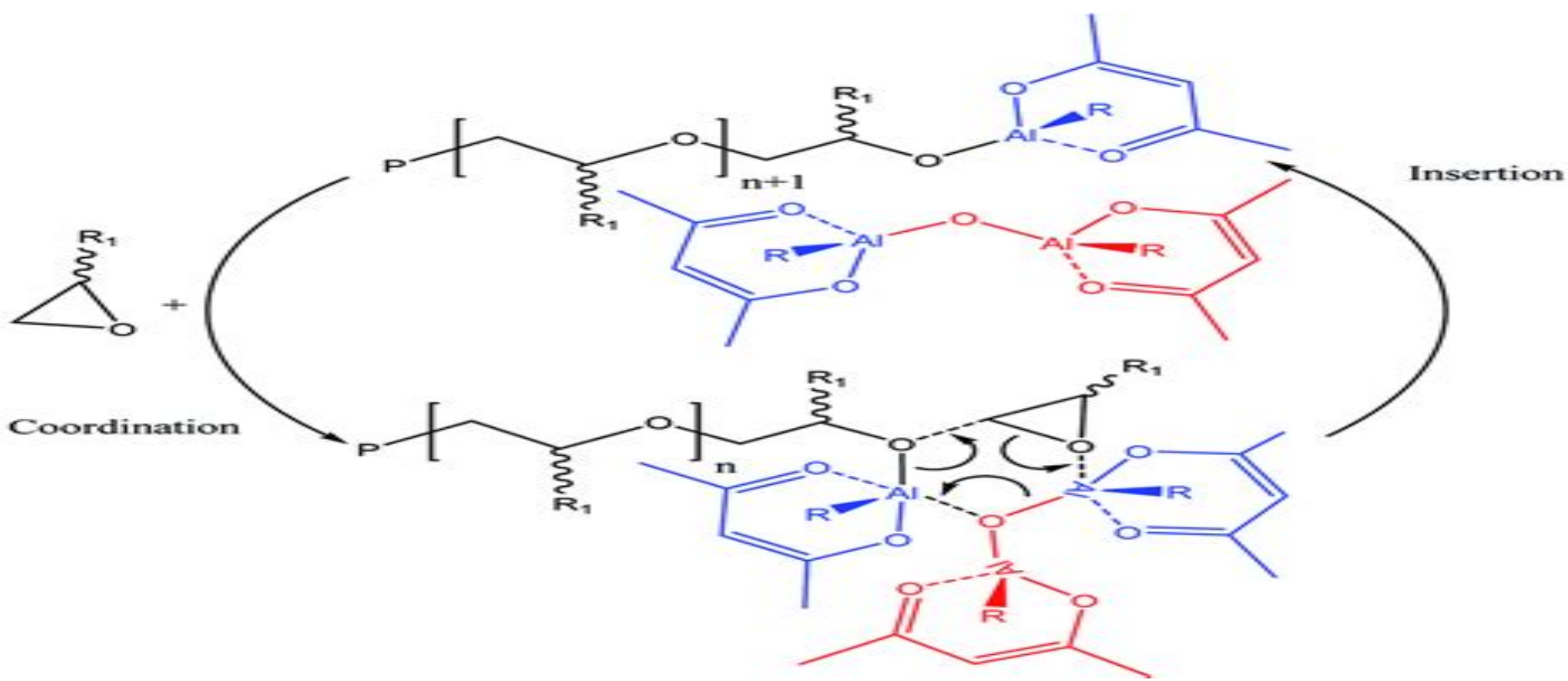


a) Initiation



b) Propagation



Ring Opening Polymerization Of Cyclotetrasilanes A Versatile Route To Linear Polysilylenes

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K. Kim, CARNEGIE-MELLON UNIV
PITTSBURGH PA DEPT OF CHEMISTRY.**

Ring Opening Polymerization Of Cyclotetrasilanes A Versatile Route To Linear Polysilylenes:

Ring Opening Polymerization of Cyclotetrasilanes: A Versatile Route to Linear Polysilylenes, 1995 This paper reviews ring opening polymerization ROP of cyclotetrasilanes The ROP of cyclotetrasilanes is an interesting and versatile method to prepare both polysilylenes homo and copolymers which cannot be prepared by other methods First fundamentals of ROP are discussed with a special emphasis on thermodynamics and kinetics as well as chemoselectivity regioselectivity and stereoselectivity Subsequently a basis of silicon chemistry including Si Si bond formation and cyclosilanes is covered A variety of cyclotetrasilanes $\text{Me}_n\text{Ph}_{8-n}\text{Si}_4$ where $n = 3, 4, 5$ or 6 were prepared and polymerized using silyl cuprates as initiators The polymerization of the all trans isomer of $\text{Me}_4\text{Ph}_4\text{Si}_4$ proceeded with two inversions of configuration at both the attacked silicon atom in the ring and the newly formed reactive center resulting in a polymer with 75% heterotactic triads and 25% isotactic triads Polymerization of the tri penta and hexamethyl derivatives proceeded with some degree of regioselectivity

pg 2 Ring Opening Polymerization of Cyclotetrasilanes Eric A. Fossum, 1995 *Handbook of Ring-Opening Polymerization* Philippe Dubois, Olivier Coulembier, Jean-Marie Raquez, 2008-12-17 This comprehensive truly one stop reference discusses monomers methods stereochemistry industrial applications and more Chapters written by internationally acclaimed experts in their respective fields cover both basic principles and up to date information ranging from the controlled ring opening polymerization methods to polymer materials of industrial interest All main classes of monomers including heterocyclics cyclic olefins and alkynes and cycloalkanes are discussed separately as well as their specificities regarding the ring opening polymerization techniques the mechanisms the degree of control the properties of the related polymers and their applications The two last chapters are devoted to the implementation of green chemistry in ring opening polymerization processes Of much interest to chemists in academia and industry

Ring-Opening Polymerization of Strained Cyclotetrasilanes as a New Route Towards Well Defined Polysilylenes, 1994 Ring opening polymerization of cyclic silanes is described as a new synthetic route to well defined high molecular weight polysilylenes polysilanes Strained cyclotetrasilanes with phenyl and methyl substituents at each Si atom in the four membered ring are prepared by partial dephenylation of octaphenylcyclotetrasilane with triflic acid and the subsequent treatment with methylmagnesium bromide Chemoselectivity regioselectivity and stereoselectivity of monomer synthesis is discussed in detail In addition to classic anionic initiators for the ring opening process new catalysts and initiators based on transition metals Cu Pd Pt are described They provide much better control of the microstructure than systems with Li counterion

The Anionic Ring-opening Polymerization of Cyclic Imines Louis Reisman, 2019 One important class of polymers is polyimines Polyimines have a wide range of applications such as CO_2 capture and non viral gene transfection Despite their many applications the use of these polymers is limited due to difficulties in controlling the polymerization To increase the feasibility of polyimines in the aforementioned high value applications the research in this dissertation focuses on controlled routes to produce linear polyimines using living anionic

ring opening polymerization AROP The early work of this dissertation focuses on an AROP route to linear polyethylenimine LPEI Due to the insolubility of p N sulfonylaziridine s i e non 2 substituted in all common solvents this was achieved using a copolymerization strategy Utilizing two N sulfonylaziridines N methanesulfonyl aziridine MsAz and N sec butylsulfonyl aziridine sBsAz with similar reactivities a soluble random copolymer with narrow molecular weight distributions is produced Removal of the sulfonyl groups of p MsAz r sBsAz affords the first example of LPEI by living controlled AROP The later work in this dissertation focuses on the AROP of N sulfonylazetidines in route to linear poly trimethylenimine LPTMI Initially the polymerization of N methanesulfonyl azetidine MsAzet was investigated The kinetics of this polymerization were studied and the reaction found to be first order with respect to monomer and the number of active chain ends remains constant throughout the polymerization Interestingly activation occurs at the methanesulfonyl group leading to polymer branching This branching precludes p MsAzet from being a precursor to LPTMI By more judicious selection of N sulfonylazetidine monomers a living controlled AROP approach to LPTMI was achieved by copolymerizing two similar N sulfonylazetidines N p tolylsulfonyl azetidine pTsAzet and N o tolylsulfonyl azetidine oTsAzet to produce a statistical copolymer Copolymerization was required as the homopolymers resulting from these monomers were insoluble in all common solvents The copolymerization is living and controlled producing polymers with narrow molecular weight distributions The kinetics of the copolymerization and the reactivity ratios of the two monomers were studied and the sulfonyl groups of the polymer were removed to provide the first example of LPTMI by living controlled AROP Finally the high barrier to polymerization of N sulfonylazetidines was utilized to produce block copolymers containing no homopolymer impurities in a closed system in which all monomers are present in solution at the time of initiation

Ring-opening Polymerization Kenneth John Ivin,Takeo Saegusa,1984

New Synthetic Routes to Polysilanes Krzysztof Matyjaszewski,Y. L. Chen,H. K. Kim,CARNEGIE-MELLON UNIV PITTSBURGH PA DEPT OF CHEMISTRY.,1987 Three new synthetic routes for the synthesis of polysilanes have been applied low temperature coupling in the presence of ultrasound modification of poly alkylarylsilylene with triflic acid and ring opening polymerization Low temperature reductive coupling of dichlorosilanes with sodium in the presence of ultrasound leads to monomodal polymers with low polydispersity in contrast to bimodal polymers prepared by the thermal coupling Modification of polysilanes with triflic acid gives access to new polysilanes with pendant alkoxy or amino substituents Ring opening polymerization have been successful only for the strained cyclic polysilanes with small substituents

Ring-opening Polymerization ,1985

Decoding **Ring Opening Polymerization Of Cyclotetrasilanes A Versatile Route To Linear Polysilylenes**: Revealing the Captivating Potential of Verbal Expression

In an era characterized by interconnectedness and an insatiable thirst for knowledge, the captivating potential of verbal expression has emerged as a formidable force. Its capability to evoke sentiments, stimulate introspection, and incite profound transformations is genuinely awe-inspiring. Within the pages of "**Ring Opening Polymerization Of Cyclotetrasilanes A Versatile Route To Linear Polysilylenes**," a mesmerizing literary creation penned by a celebrated wordsmith, readers set about an enlightening odyssey, unraveling the intricate significance of language and its enduring effect on our lives. In this appraisal, we shall explore the book's central themes, evaluate its distinctive writing style, and gauge its pervasive influence on the hearts and minds of its readership.

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