

Chapter 1 : Polymerization of Alkenes - Chemistry LibreTexts

Principles of Coordination Polymerisation, is one of the firstbooks to offer a unified and almost complete view of coordinationpolymerisation. It focuses on the polymerisation of monomers,belonging to all the important classes of hydrocarbons andnon-hydrocarbon monomers, in the presence of various kinds ofcoordination catalysts.

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 C₂ 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 2 : Principles of Coordination Polymerisation - Download Free EBooks

The first all-inclusive text covering coordination polymerisation, including important classes of non-hydrocarbon monomers. Charting the achievements and progress in the field, in terms of both basic and industrial research, this book offers a unified and complete overview of coordination polymerisation.

Thus polymerization of propene gives a long-chain hydrocarbon with recurring units: Alkene Monomers and Their Polymers Most technically important polymerizations of alkenes occur by chain mechanisms and may be classed as anion, cation, or radical reactions, depending upon the character of the chain-carrying species. In each case, the key steps involve successive additions to molecules of the alkene, the differences being in the number of electrons that are supplied by the attacking agent for formation of the new carbon-carbon bond. For simplicity, these steps will be illustrated by using ethene, even though it does not polymerize very easily by any of them: Attack by the carbanion on another alkene molecule would give a four-carbon carbanion, and subsequent additions to further alkene molecules would lead to a high-molecular-weight anion: The growing chain can be terminated by any reaction such as the addition of a proton that would destroy the carbanion on the end of the chain: Anionic polymerization of alkenes is quite difficult to achieve because few anions or nucleophiles are able to add readily to alkene double bonds see Section Anionic polymerization occurs readily only with alkenes substituted with sufficiently powerful electron-attracting groups to expedite nucleophilic attack. By this reasoning, alkynes should polymerize more readily than alkenes under anionic conditions, but there appear to be no technically important alkyne polymerizations in operation by this or any other mechanism. Perhaps this is because the resultant polymer would be highly conjugated, and therefore highly reactive, and may not survive the experimental conditions: Then, in the absence of any other reasonably strong nucleophilic reagent, another alkene molecule donates an electron pair and forms a longer-chain cation. Continuation of this process can lead to a high-molecular-weight cation. Termination can occur by loss of a proton. The following equations represent the overall reaction sequence: Ethene does not polymerize by the cationic mechanism because it does not have sufficiently electron-donating groups to permit easy formation of the intermediate growing-chain cation. The usual catalysts for cationic polymerization of 2-methylpropene are sulfuric acid, hydrogen fluoride, or a complex of boron trifluoride and water. Under nearly anhydrous conditions a very long chain polymer called polyisobutylene is formed. Polyisobutylene fractions of particular molecular weights are very tacky and are used as adhesives for pressure-sealing tapes. The proton can be lost in two different ways, and a mixture of alkene isomers is obtained. The alkene mixture is known as "diisobutylene" and has a number of commercial uses. The initiation step involves formation of radicals, and chain propagation entails stepwise addition of radicals to ethene molecules. Chain termination can occur by any reaction resulting in combination or disproportionation of free radicals. The polymer possesses a number of desirable properties as a plastic and is used widely for electrical insulation, packaging films, piping, and a variety of molded articles. Propene and 2-methylpropene do not polymerize satisfactorily by radical mechanisms. Ethene also polymerizes quite rapidly at atmospheric pressure and room temperature in an alkane solvent containing a suspension of the insoluble reaction product from triethylaluminum and titanium tetrachloride Ziegler process. Both the Phillips and Ziegler processes produce very high-molecular-weight polyethene with exceptional physical properties. The unusual characteristics of these reactions indicate that no simple anion, cation, or radical mechanism can be involved. It is believed that the catalysts act by coordinating with the alkene molecules in somewhat the same way that hydrogenation catalysts combine with alkenes Section A. Polymerization of propene by the Ziegler process gives a very useful plastic material. It can be made into durable fibers or molded into a variety of shapes. A Nobel Prize was shared in by K. Natta for their work on alkene polymerization. The properties and uses of polymers are discussed in greater detail in Chapters 13 and The most important alkene monomers used in addition polymerizations are listed in Table along with some names and uses of the corresponding polymers. Robert and Marjorie C. Caserio Basic Principles of Organic Chemistry, second edition. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution,

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Chapter 3 : Principles of Coordination Polymerization - PDF Free Download

The first all-inclusive text covering coordination polymerisation, including important classes of non-hydrocarbon monomers. Charting the achievements and progress in the field, in terms of both basic and industrial research, this book offers a unified and complete overview of coordination.

For the last 25 years of his life he was a professor at the Faculty of Chemistry Warsaw University of Technology, where he chaired the Division of Polymer Synthesis and Processing. During his early studies he became fascinated with the discoveries of Karl Ziegler and Giulio Natta and the great opportunities provided by organometallic catalysts for the progress of the chemistry and technology of high polymers, and he concentrated on this subject throughout his professional life. Studies of the reactions of organoaluminium and organozinc compounds and the utilisation of these derivatives as catalysts in polymerisation processes of polar vinyl and heterocyclic monomers were the main focus of his work. In the mid-50s he began to study the copolymerisation of carbon dioxide with heterocyclic monomers. In a short time, the team led by him developed a number of original and very active catalysts for these processes. During further studies it appeared that these catalysts could be successfully applied in the coordination polymerisation of oxiranes, cyclic carbonates and other heterocyclic monomers. His own broad experimental results and also extremely precise analysis of the results published by other researchers made it possible to form a general concept of organometallic catalysis in the polymerisation of heterocyclic monomers, which he presented in a number of monographic publications. He is the coauthor of fundamental works on palladium 0 complexes, which appeared during his fellowship in the school of Giulio Natta in Milan, and also of many works devoted to the utilisation of cyclic carbonates in the synthesis of condensation polymers. The systematic deterioration in the health of Professor Kuran was also a key factor in slowing down the work on the book. We hope that the small changes introduced by us do not disturb the original concept of the author, who was our teacher and friend, and that the great work of his life will prove to be useful both to students and to those professionally involved in polymer chemistry and technology. Actually, only a few existing textbooks contain individual chapters connected with coordination polymerisation. The spectacular breakthrough made possible by these discoveries, honoured with the Nobel Prize in 1958, revolutionised polymer science and technology in the second half of the twentieth century. We are now witnessing the next phase of this revolution, which was initiated, in the mid-60s, by the discoveries of metallocene single-site catalysts which could be tailored to produce polymers of virtually all feasible microstructures. These achievements offer attractive potential for the development of basic research in terms of mechanistic studies as well as for the introduction of new or improved industrial processes in various branches of the plastics and rubber industries. Thus, the lack of a suitable textbook lessens the chance of proper mastery of the important discipline of coordination polymerisation, and the training that most chemists receive seems to be inadequate, which is deplorable. It arose from the need for a text, devoted to coordination polymerisation, to accompany introductory courses as well as advanced courses in polymer science, catalysis and in polymerisation catalysis. It is thought to be useful for research students and research workers in industry, and will also be helpful as a reference book. The main inspiration that has enabled me, after many years, to prepare this book has been my constant interest in coordination polymerisation. Successively collected literature data, my own studies and the results of work carried out in the Institute of Organic Chemistry and Technology and the Division of Polymer Synthesis and Processing at the Faculty of Chemistry, Warsaw University of Technology, headed by me, were of assistance in the preparation of this work. The textbook is focused on the polymerisation of monomers belonging to all the important classes of hydrocarbon as well as non-hydrocarbon monomers, in the presence of coordination catalysts of various kinds, and emphasises the growing importance of coordination polymerisation for basic research as well as for industrial processes. A vast amount of material, covering coordination polymerisation almost in its entirety and considering the whole range of monomers susceptible to polymerisation with coordination catalysts and the whole range of respective more important coordination catalysts, has been collected and selected conscientiously to suit readers with various levels and breadths of knowledge of the

subject. Considering that several generations of catalysts and processes have been introduced on a commercial scale to produce a large variety of most widespread polymeric materials ranging from commodity thermoplastics to rubbers, to some extent the emphasis is laid on the coordination polymerisation of alkenes, particularly of 1,3-dialkenes, in the textbook. The contents of the book are systematised, taking into account basic features of the mechanisms that operate in coordination polymerisations of various monomers and depend on the kind of monomer and catalyst. This is, essentially, consistent with the alignment of monomers according to their properties resulting from their structure. Finally, Chapter 9 is concerned with the coordination polymerisation of non-hydrocarbon monomers, such as heterocyclic and heterounsaturated monomers. Taking the above into consideration, the individual chapters of the book are not equal, but differ in volume according to the importance and breadth of the problems presented as regards the chemistry rather than the technology. Problems are listed at the end of each chapter in order to enable students or other readers to absorb its contents more easily. Taking into account one of the most important features of coordination catalysts, which is their capability of producing stereoregular polymers, when discussing the polymerisation of individual groups of monomers, special attention is paid to the structures of the catalyst active species and the stereocontrol mechanism of these polymerisations. These key questions for an understanding of the nature of coordination polymerisation are treated with special emphasis in the textbook, especially when considering that the utility of coordination polymerisation for producing stereoregular polymers is well established. The idea is for the text to be eminently teachable for instructors and easily comprehensible for students. By far the majority of colleges and universities have no courses in coordination polymerisation, no staff member conducting research in this area and only cursory mention of xviii PREFACE polymers in other courses. There are, needless to say, many exceptions, ranging from the isolated effort of a single staff member to such major centres for polymer research as those where a dozen or more staff members constitute a formal or informal polymer research group. The approach to referencing the literature in the book is such that the most recent bibliography is cited as References, including most of the latest review articles and books; the most important original works are also listed, however. More general reviews and book chapters are also listed as Further Reading. In order to avoid a long list of References and Further Reading at the end of the textbook, they are listed at the end of each individual chapter. The book is intended for MSc and PhD students in catalysis, and in polymerisation catalysis, for undergraduate and research students in polymer science in general, for college and university instructors and for industrial researchers. Principles of Coordination Polymerisation. The application of physical methods to investigate such materials as rubbers, polysaccharides or proteins as recently as the twentieth century, demonstrating that these materials are characterised by large molecular weights, did not prompt scientists to conclude that they are built from large molecules. This view was still held as late as the end of the s, one decade later, when Staudinger proposed that polymeric materials were actually composed of giant molecules that he called macromolecules [1]. At this juncture, when problems connected with the nature of polymeric molecules and with the explanation of their structure were the most important problems engaging the minds of investigators, the concept of the mechanism in chemistry as a whole was hardly developed. This matters, of course, when considering that natural rubber, which is a relatively simple polymeric substance, has attracted the attention of scientists for nearly one century. Watson and Crick [5] for their discovery of the double helical architecture of DNA. We should realise, however, that, for reactions concerning the formation of macromolecular systems, the same laws are obeyed as those governing systems consisting of low molecular weight substances with which organic chemistry deals, and there can be no dichotomy of mechanisms and structures in terms of their division into polymer chemistry and organic chemistry. However, stereochemical problems are of particular interest in coordination polymerisation, since this polymerisation often leads to stereoregular polymers which is not the common case in other polymerisations. Owing to the tremendous development of spectroscopic techniques, it has become possible to investigate the stereoisomerism in polymers, which concerns both natural and synthetic polymers. Cellulose, the most abundant naturally occurring polymer its annual growth on earth is estimated to be in the region of 10^{10} t, appeared to be 1,4-threo-disyndiotactic poly D-glucopyranose or, as we know from organic chemistry, the polymer of D-glucopyranose containing b-1,4-D-glucopyranoside units [8]. These new metallocene-based

catalysts essentially consist of one type of catalytically active site, which may be tailored to polymerise hydrocarbon monomers to polymers that can be characterised by virtually all feasible microstructures. This also concerns syndiotactic polystyrene which can be easily obtained with metallocene-based catalysts. Moreover, microstructure, molecular weight, end-group composition and comonomer incorporation can be varied independently when polymerising hydrocarbon monomers with metallocene-based catalysts. In contrast to multisite supported catalysts, the novel generation of metallocene single-site catalysts creates greater possibilities of gaining an insight into the basic reaction mechanisms accounting for stereochemical and molecular weight control. The versatility of metallocene and other single-site catalysts found and developed recently will likely result in their utilisation in a wide range of polymerisation processes in industry. It is clear that the potential of metallocene and related polymerisation coordination catalysts has been only partially exploited [19]. Conjugated diene polymerisation processes with coordination catalysts have not been developed to such an extent as those concerning monoalkenes. The recent landmark discoveries offer attractive potential for the development of new and environmentally harmless versatile classes of hydrocarbon-based polymeric materials and expand the frontiers of polymer technology. However, extensive mechanistic studies on these processes as well as exploratory investigations for obtaining better, especially highperformance catalysts in terms of commercial development aspects, are constantly being carried out. The application of coordination catalysts for the polymerisation of heterocyclic monomers has broadened the synthetic feasibility of these polymerisations as regards the possibility of obtaining high molecular weight homopolymers that may be characterised by a high degree of regio- and stereoregularity, and the possibility of obtaining high molecular weight copolymers with heterounsaturated monomers such as, for example, carbon dioxide [33] that cannot be obtained in other ways [34]. A very important aspect of the coordination polymerisation of heterocyclic monomers is connected with certain advantageous properties of the polymers obtained from such monomers as potentially useful materials for biomedical and pharmaceutical applications in terms of their low toxicity and favourable biodegradability. Note in this connection the friendly environmental behaviour of polymers derived from such monomers. Thus, the coordination polymerisation and copolymerisation of heterocyclic and heterounsaturated monomers has also acquired great importance, although such polymerisation has other purposes [34] than those concerning the coordination polymerisation of hydrocarbon monomers. Although coordination polymerisation is characterised by a relatively short period of development as a branch of polymer chemistry, it is making a major contribution towards the further development of polymer science. As nature affords us macromolecules, with some characterised by certain useful INTRODUCTION 5 properties and others, being isomeric to them, characterised by completely different usable features, so modern technology has started to afford stereoisomers of synthetic polymers that exhibit new valuable properties. Acta, 5, Further Reading Morawetz, H. What are the milestones determining polymer chemistry development? Why is there no dichotomy between the mechanisms governing reactions proceeding in low molecular weight and high molecular weight systems? What is coordination polymerisation and what are its most characteristic features? Which groups of monomers undergo coordination polymerisation? What are the advantages of coordination polymerisation? Explain why coordination polymerisation revolutionised the plastics and rubber industries. This implies that the growing polymer chain is covalently bound to the metal atom.

Chapter 4 : Coordination polymerization - Wikipedia

Principles of Coordination Polymerisation / Edition 1 The first all-inclusive text covering coordination polymerisation, including important classes of non-hydrocarbon monomers. Charting the achievements and progress in the field, in terms of both basic and industrial research, this book offers a unified and complete overview of coordination.

Chapter 5 : principles of polymerization | Download eBook PDF/EPUB

This text covers coordination polymerisation, including important classes of non-hydrocarbon monomers. It charts the

achievements and progress in the field, in terms of both basic and industrial.

Chapter 6 : The Organometallic HyperTextBook: Olefin Polymerization

Coordination Polymerisation of Non-hydrocarbon (Heterocyclic and Heterounsaturated) Monomers Monomers and Catalysts Polymerisation of Oxacyclic Monomers Polymerisation of Cyclic Ethers Stereoisomerism of Epoxide Polymers Catalysts for Polymerisation of Epoxides Mode of Epoxide Ring Opening Models of.

Chapter 7 : Radical polymerization - Wikipedia

Coordination polymerization is another variant of chain-growth polymerization. The kinetic chain starts with addition of monomer to a metal complex, propagation is by successive insertion of monomer at the metal, and termination occurs when the metal complex separates from the polymer.