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Polyisobutylene succinic anhydride (PIBSA) is a versatile chemical compound used in various industrial applications. It is derived from the reaction of polyisobutylene with maleic anhydride. PIBSA finds utility as a lubricant additive, dispersant, and emulsifier in industries such as automotive, lubricants, oilfield chemicals, and more. Here's a
comprehensive guide to understanding PIBSA: Chemical Structure: Polyisobutylene succinic anhydride (PIBSA) is typically represented by the following chemical formula: PIB+Maleic Anhydride is often a pale yellow to amber-colored liquid.
Molecular Weight: Varies depending on the degree of polymerization of the polyisobutylene used in its productions. Acid Value: Measures the amount of acidic functional groups in PIBSA and influences its reactivity and performance in applications. Applications: Lubricant
Additive: Polyisobutylene succinic anhydride is used as a dispersant and detergent in lubricants to prevent the formation of deposits, inhibit corrosion, and improve the overall performance of the lubricants to prevent the formation of deposits, inhibit corrosion, and improve the overall performance of the lubricants. It enhances the dispersant and detergent in lubricants to prevent the formation of deposits, inhibit corrosion, and improve the overall performance of the lubricants.
equipment life. Fuel Additive: In fuel formulations, PIBSA functions as a dispersant and detergent to maintain engine cleanliness, improve fuel efficiency, and combustion chambers. Emulsifier: Polyisobutylene succinic anhydride is employed as an emulsifier
in various industrial processes, particularly in the production of emulsifiable concentrates for agricultural pesticides and herbicides. It facilitates the formation and stabilization of oil-in-water emulsions, improving the dispersibility and effectiveness of active ingredients. Corrosion Inhibitor:Polyisobutylene succinic anhydride is utilized as a corrosion
inhibitor in metalworking fluids, hydraulic fluids, and rust preventives to protect metal surfaces from degradation caused by moisture and coatings Personal care products Paper and pulp industry Benefits: Improved Performance: Enhances the performance and longevity of
lubricants, fuels, and other formulated products. Cleanliness in engines and equipment by preventing the service life of machinery, thereby promoting sustainability. Safety Precautions: Polyisobutylene succinic
anhydride should be handled in accordance with safety guidelines, including wearing appropriate personal protective equipment (PPE). Adequate ventilation and containment measures should be in place to prevent exposure and minimize environmental impact. Conclusion: Polyisobutylene succinic anhydride is a multifunctional additive with
widespread applications in various industries. Its ability to enhance lubricant performance, maintain engine cleanliness, and improve the effectiveness of formulated products makes it indispensable in modern manufacturing and maintenance processes. Understanding its properties, applications, and safety considerations is crucial for maximizing its
benefits while ensuring safe handling and use. PIBSA 1000, also known as Polyisobutylene Succinic Anhydride with an average molecular weight of 1000, isn't directly used as an additive but serves as a crucial building block in the synthesis of several essential lubricant additives, particularly ashless dispersants. PIBSA 1000 is a lubricant additive
intermediate prepared from high reactive polyisobutylene (Mn=1000) by thermal adduction process. The ashless dispersant produced from PIBSA1000 possesses fine detergency and favourable low temperature sludge dispersant. Used for
preparation of emulsifying agents for emulsion explosives. Used for preparation of processing aids for petroleum chemical plant In the context of industrial chemicals and additives, manufacturers often use numerical codes or designations to classify different grades or variants of a particular compound. These codes are used to differentiate between
products with specific properties or applications. Here's a comprehensive dive into PIBSA 1000: Chemical Makeup: PIBSA 1000 is a molecule formed by attaching succinic anhydride groups to the end of polyisobutylene (PIB) chains, with an average molecular weight of approximately 1000. Function: PIBSA 1000 acts as a reactive intermediate. It's a
starting material for the synthesis of Polyisobutylene Succinimide (PIBSI), a key component in many lubricant additives. Synthesis of PIBSI is formed by the reaction of PIBSI is formed by the reaction of PIBSI is formed by the reaction of PIBSI derived from
PIBSA 1000: Ashless dispersants: These are vital additives in various lubricants, including: Engine oil Gear oil Hydraulic oil Automatic transmission fluid (ATF) Function of ashless dispersants: Maintain engine cleanliness by suspending contaminants and sludge particles within the oil. Prevent them from settling and agglomerating into harmful
deposits. Contribute to:Reduced wear and tear on engine components Extended engine life Improved fuel efficiency Benefits of using PIBSA 1000-derived PIBSI as an ashless dispersant: Excellent dispersing ability even
under high shearing forces within the engine. Compatibility: Compatible with various base oils and other lubricants. The selection of the appropriate
ashless dispersant based on PIBSA 1000) depends on various factors like: The type of lubricant components Consulting a qualified tribologist (friction and wear specialist) or lubricant manufacturer is crucial for choosing the most suitable ashless dispersant
based on PIBSA 1000 or other precursors, considering your specific application needs. Additional Points: PIBSA 1000 is available in various grades and formulations with different properties catering to specific applications. The proper handling and storage of PIBSA 1000 are crucial due to its chemical properties. Always follow the manufacturer's
safety data sheet (SDS) guidelines. In conclusion, PIBSA 1000 plays a significant indirect role in modern lubricant technology by serving as a key intermediate in the production of high-performance ashless dispersants. These dispersants are essential for maintaining engine cleanliness, reducing wear, and extending lubricant life. Shanghai Minglan
Chemical Co., Ltd. is a professional manufacturer and supplier of lubricant additives. We have committed to supply the professional, perfect, effective and satisfactory lubrication solutions all the time. Our lubricant additive packages meet the specification requirement of bunch test, and possess excellent product performance and reliable quality, so that
always holds technology leading status in the lubrication industry. We are specialized in supplying high-quality lubricant additive, antiodant, viscosity index improver, rust inhibitor, Pour Point Depressant, engine oil additive package,
gear oil additive package, hydraulic oil additive package and so on. If you are interested in the PIBSA1000, I recommend reaching out to us, we can provide more detailed information about our product Introduction. Product Introduction Polyisobutylene
Succinic Anhydride is a lubricant additive intermediate prepared from high reactive polyisobutylene (Mn=1000) by thermal adduction process. The ashless dispersion. Polyisobutylene Succinic Anhydride is a type of polyisobutylene succinic anhydride
also known as thermal adduction PIBSA. Polyisobutylene, a synthetic polymer. PIBSA is produced by reacting polyisobutylene with maleic anhydride, resulting in the formation of succinic anhydride groups on
the polymer chain. PIBSA is used as a dispersant, detergent, and corrosion inhibitor in lubricants. It helps to prevent the formation of sludge and deposits in engines, improving their overall performance and efficiency. It also reduces corrosion and wear on engine components. In addition to being used in lubricants, PIBSA can also be used as a
viscosity index improver, which helps to maintain consistent lubricant viscosity over a wide range of temperatures. It can also be used as a coupling agent and emulsifier in various applications. Overall, PIBSA is a versatile and effective additive that helps to enhance the performance and durability of lubricants in a range of applications. Special
features Free of chlorine Applications Used for preparation of polyisobutylene diene and polyene succinimide and bononize ashless dispersant. Used for preparation of processing aids for petroleum chemical plant Item Typical Value Test Method Appearance Transparent Viscous
Liquid Visual Density(20°C),kg/m³ 900-1000 SH/T0604,ASTM D445 Saponification Value,mg KOH/g >80 GB/T3536,ASTM D92 Kinematic Viscosity(100°C),mm²/s Report GB/T265,ASTM D445 Saponification Value,mg KOH/g >80 GB/T8021,ASTM D94 Free Anhydride,m% \leq0.7 MechanicalImpurities,m% \leq0.2 GB/T511 Company OverviewAt [Shanghai Minglan Company OverviewAt
Chemical Co., Ltd.], we specialize in high-performance lubricant additive packages, helping manufacturers develop next-generation engine oils, industrial lubricants, and regulatory compliance assistance, ensuring your products
meet API, ACEA, ILSAC, and OEM standards. We leverage cutting-edge chemistry and extensive field testing to optimize oxidation stability, wear protection, fuel economy, and emissions control. Our modular additive systems allow formulators to customize viscosity, friction characteristics, and deposit control properties for specific market needs.
Partnering with us means gaining access to expert technical support, innovative additive technologies, and a long-term strategy for staying ahead in the lubricants, we provide the expertise, resources, and reliability you need to succeed. Laboratory Arrangement
Factory pictures Polyisobutylene succinic anhydride (PIBSA) is an important intermediate used in the production of various lubricants but plays a crucial role in creating other functional components. Here's a breakdown of Polyisobutylene Succinic Anhydride: Structure: PIBSA consists of a polyisobutylene succinic anhydride (PIBSA) is an important intermediate used in the production of various lubricants but plays a crucial role in creating other functional components.
(PIB) backbone, which is a synthetic rubber-like polymer, with a succinic anhydride group attached at one end. How Polyisobutylene Succinic Anhydride is Used: PIBSA is a key building block for the synthesis of several lubricant additives, particularly: Ashless Dispersants: These are a vital category of additives that help keep engine oil clean by
suspending contaminants like soot, sludge, and varnish particles within the oil. They prevent these contaminants from agglomerating and depositing on engine components, maintaining oil cleanliness and performance. Detergents: PIBSA-derived detergents can further enhance oil cleanliness by removing contaminants and dispersing them within the
oil. Production Process: PIBSA is typically produced by reacting polyisobutylene with maleic anhydride through a chemical process. The molecular weight of the PIB used can be varied to obtain PIBSA with different properties, influencing the performance of the final dispersant or detergent additives derived from it. Benefits of Using PIBSA-Derived
Additives: Improved Engine Cleanliness: Ashless dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersing contaminants. Reduced Wear: Cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersants and detergents made from PIBSA contribute to cleaner engines by effectively suspending and dispersant engines are contributed as a suspending and dispersant engines are contributed by effectively suspending and dispersant engines are contributed as a suspending as a suspending and dispersant engines are contributed as a suspending and dispersant engines are co
oil cleanliness and performance, PIBSA-derived additives can help extend oil drain intervals. Friction Reduction: Cleaner engines with less friction can potentially experience some improvement in fuel efficiency. Environmental Considerations: While PIBSA itself isn't directly used in lubricants, the disposal of lubricating oils containing PIBSA-derived
additives needs to be done responsibly following recommended practices. Overall, Polyisobutylene Succinic Anhydride plays a significant role in the production of modern ashless dispersants and detergents, which are essential for clean and efficient engine operation. Forsberg JW. Water-in-oil emulsions. US Patent 4,708,753. 1987. Chattopadhyay AK.
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Polym Anal Charact. 1995;1(1):3-34. doi:10.1080/10236669508009704. Article CAS Google Scholar RB Products manufactures and supplies an extensive line of additive componentry products, which provide performance enhancements when added to a chosen base oil mixture. RB PIBSA is a polyisobutylene succinic anhydride (PIBSA) derived from
highly-reactive, 1000 molecular weight polybutene. It is produced via a chlorine-free thermal process. RB PIBSA is commonly used as an intermediate in the manufacturing of emulsifiers for various applications, including explosives and metalworking. Synonyms for
Polyisobutylene Succinic Anhydride (PIBSA) 2,5-Furandione, Dihydro-, Monopolyisobutylene Derivs 5-Furandione, Dihydro-, Monopolyisobutylene Derivs 5-Furandione
today! Physical PropertyUnitTest MethodTypical Value Specific Gravity (60°F) °F ASTM D 4052 0.92 Viscosity (100°C) cSt ASTM D 4052 0.92
Anhydride (PIBSA) In the realm of lubricant and fuel additives, Polyisobutylene Succinic Anhydride (PIBSA) stands out as a versatile and essential chemical compound. Widely used across various industries, PIBSA plays a pivotal role in enhancing the performance and longevity of engines and machinery. This article delves into what PIBSA is, its
chemical structure, properties, applications, and the myriad benefits it offers. Whether you're in the automotive, industrial, or specialty chemical sector, understanding PIBSA can provide valuable insights into improving operational efficiency. PIBSA is an acronym for Polyisobutylene Succinic Anhydride, a chemical intermediate derived from the
reaction of polyisobutylene (PIB) with maleic anhydride. PIBSA serves as a foundational building block in the production of lubricant additives, particularly dispersants and detergents that keep engines clean and running smoothly. PIBSA's chemical structure features a polyisobutylene backbone bonded to succinic anhydride groups. This unique
configuration imparts several important properties: Reactivity: The succinic anhydride groups are highly reactive, allowing PIBSA to bond with various chemicals to form derivatives like succinimides and esters. Oil Solubility: The hydrophobic polyisobutylene chain ensures excellent solubility in oils and fuels. Viscosity Improvement: It contributes to
solubility and reactivity. Succinic Anhydride Content: Determines the degree of functionality in additive applications. Viscosity: Impacts the handling and blending processes. PIBSA is composed primarily of:Polyisobutylene (PIB): A polymer of isobutylene with varying molecular weights. Maleic Anhydride: Reacts with PIB to form the succinic anhydride
groups. A typical PIBSA specification sheet includes; Appearance: Viscous amber liquid. Acid Number: Indicates the amount of succinic anhydride groups. Saponification Number: Reflects the total acid functionality. Viscosity: Measured in centistokes (cSt) at a standard temperature, usually 100°C. PIBSA is also known by other names,
including:Polybutenyl Succinic AnhydridePIB 
deposits within engines. Viscosity Index Improvers: Enhances fuel economy and power output. Reduce Emissions: Lowers harmful exhaust emissions by promoting complete combustion. Prevent Deposit
Formation: Keeps fuel injectors and intake valves clean. Beyond fuels and lubricants, PIBSA finds applications in: Metalworking Fluids: Acts as an emulsifier and corrosion inhibitor. Adhesives and Sealants: Improves adhesion properties. Surfactants and Emulsifiers: Used in the formulation of cleaning agents. The use of PIBSA offers numerous
advantages across different applications.PIBSA serves multiple functions: Enhances Lubricant Properties: Improves viscosity and thermal stability. Boosts Fuel Quality: Enhances combustion characteristics. As a detergent and dispersant, PIBSA: Prevents Sludge Formation: Keeps contaminants suspended in the lubricant. Maintains Engine Cleanliness
Extends engine life and performance.PIBSA provides corrosion inhibition by:Forming Protective Layers: Shields metal surfaces from combustion byproducts. By improving lubricity, PIBSA:Minimizes Metal-to-Metal Contact: Reduces wear on engine components. Enhances Efficiency:
Leads to smoother engine and machinery operation. PIBSA helps in: Viscosity Stabilization: Ensures consistent performance in varying temperatures. Lubricity Enhancement: Improves the lubricant's ability to reduce friction. Proper safety measures are essential when handling PIBSA. Irritation Risk: Can cause skin and eye irritation upon
contact. Environmental Impact: Should be prevented from entering waterways. Personal Protective Equipment (PPE): Use gloves, goggles, and protective clothing. First Aid Measures: In case of contact, wash affected area with plenty of water. Storage: Keep in a cool, dry place away from direct sunlight. Handling: Avoid spills and use appropriate
containers. Understanding market dynamics is vital for procurement. Competitive Pricing: Offered based on market conditions and order volume. Bulk Orders: Discounts available for large quantities. Global Shipping: Logistics support for international deliveries. Compliance: Adheres to international trade regulations and standards. Contact Us: Reach
out via email or phone to discuss your needs. Customized Quotes: We provide tailored pricing based on your specifications. Technical Support: Our team can assist with technical data and product selection. Sample Requests: Available upon request for evaluation purposes. Order Confirmation: We ensure all details are agreed upon before
processing.Payment Terms: Flexible options to suit your procurement policies.Delivery Schedule: Timely shipping arrangements to meet your deadlines.For sales and technical support, contact us:Email: info@elongkang.comPIBSA
stands for Polyisobutylene Succinic Anhydride, a chemical compound used primarily as an additive in lubricants and fuels to improve performance. PIBSA is produced by reacting polyisobutylene (PIB) with maleic anhydride in a process called maleation, resulting in a molecule with succinic anhydride functional groups. PIBSA acts as a detergent and
dispersant, preventing sludge and deposits, improving viscosity, enhancing lubricity, and providing corrosion protection. It keeps contaminants suspended in the lubricant or fuel, preventing them from forming deposits that can impair engine or machinery performance. PIBSA forms a protective film on metal surfaces, shielding them from corrosive
substances and neutralizing acidic compounds. Yes, by enhancing the lubricity of oils, PIBSA reduces friction between moving parts, thereby decreasing wear and extending equipment life. PIBSA contributes to viscosity improvement, ensuring that lubricants remain effective across a wide temperature range. Lubricity refers to a fluid's ability to
minimize friction. PIBSA enhances lubricity by improving the oil's film strength, reducing metal-to-metal contact. Yes, PIBSA is used in fuels to improve combustion efficiency, reduce emissions, and prevent deposit formation in fuel systems. There are various PIBSA derivatives, such as PIBSA-succinimides and PIBSA-esters, each tailored for specific
applications like engine oils, hydraulic fluids, and fuel additives. Industries including automotive, marine, industrial machinery, and specialty chemicals utilize PIBSA in lubricants, fuels, and other products. Yes, it is important to use appropriate PPE, avoid skin and eye contact, and follow proper storage and handling guidelines as outlined in the safety
data sheet. Antioxidants Viscosity Index Improvers Anti-wear Agents PIBSAUsed as emulsifiers and durability. Customized chemical formulations to meet specific industrial requirements. PIBSA TDS and MSDS:
Available upon request to provide detailed product information. Product Catalogs Application Guides Technology Co., Ltd. is a leading manufacturer and supplier of high-quality lubricant and fuel additives, including
PIBSA. With a commitment to innovation and excellence, we serve clients worldwide, providing solutions that enhance efficiency and performance. Advanced Production Facilities: Equipped with modern technology to ensure product consistency. Strategic Location: Based in Jiangyin, China, facilitating efficient logistics and global distribution. Email:
info@elongkang.comTel.: +86 18121501731Address: No.11 Sandun East Road, Zhouzhuang, Jiangyin, ChinaWebsite: www.elongkang.comOur team is dedicated to providing exceptional customer service and technical support. Contact us to learn how our PIBSA products can benefit your operations. Unlock the potential of your lubricants and fuels
with high-quality PIBSA from Jiangyin Longkang Technology Co., Ltd. Enhance performance, efficiency, and protect your machinery by leveraging our expertise in the diesel and lubricant additives industry. Disclaimer: This article is intended for informational purposes only. For specific applications and technical guidance regarding PIBSA, please
consult with our experts. As a library, NLM provides access to scientific literature. Inclusion in an NLM database does not imply endorsement of, or agreement with, the contents by NLM or the National Institutes of Health. Learn more: PMC Disclaimer | PMC Copyright Notice . 2023 Aug 15;15(16):3415. doi: 10.3390/polym15163415 The
polymerization of isobutylene allows us to obtain a wide spectrum of polyisobutylenes (PIBs) which differ in their molecular weights (Mn
 < 5 kDa). HRPIBs are feedstocks that are in high demand in the manufacturing of additives for fuels and oils, adhesives, detergents, and other fine chemicals. In addition, HRPIBs and CMe2Cl-terminated PIBs are intensively studied with the aim of finding biomedical applications and for the purpose of developing new materials. Both chain control
(molecular weight and dispersity) and chemoselectivity (formation of exo-olefinic or -CMe2Cl groups) should be achieved during polymerization. This review highlights the fundamental issues in the mechanisms of isobutylene polymerization. This review highlights the fundamental issues in the mechanisms of isobutylene polymerization.
functionalization and applications of HRPIBs and halogen-terminated PIBs. Keywords: cationic polymerization, exo-olefinic group, highly reactive polyisobutylene, isobutylene, isobutylene, polymer functionalization, succinic anhydrides, succinimides The polymerization of isobutylene (IB) has been used in the production of high- (Mn > 100 kDa) and medium- (Mn
= 40-100 kDa) molecular weight (MW) polyisobutylenes (PIBs) and IB/isoprene copolymers (butyl rubber) [1,2,3]. Due to their remarkable impermeable property, PIBs are extensively used in many applications, such as the inner tubes and layers of tires [4]. However, the low-MW PIB (Mn < 5 kDa), possessing the exo-olefinic end-group -C(Me)=CH2,
holds the major share in the PIB market (more than 70% [2]). The PIB market was valued at USD 2.87 billion by 2028; it is expected to grow at an annual rate of 4.4% from 2021 to 2028. BASF, Braskem S.A., Chevron, Daelim Industrial Petrochemical Division, INEOS, Infineum, Kemat Polybutenes
Kothari Petrochemicals, Lubrizol Corp., SIBUR Holding, and TPC Group are the key players in the global PIB market [4]. Recently, in response to the rising global demand for high-quality medium-molecular weight PIBs, the leading chemical companies have increased their production capacity for these polymers [6,7]. Low-MW PIBs have been widely
used in the production of different fine chemicals, the bulk of which are ashless dispersants for motor oils and fuels. PIB-based dispersants represent bis-PIB succinimides (bPIB-SI); their synthesis includes two stages (Scheme 1), viz. the Alder-ene reaction between PIB and maleic anhydride (MA) with the formation of polyisobutylene-succinic
anhydrides (PIB-SAs), followed by the reaction of the PIB-SAs with H2N(CH2CH2NH) nCH2CH2NH) nCH2CH2NH) nCH2CH2NH2 (n = 1-4) and other amines [8,9,10]. The rate of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction depends significantly on the structure of the Alder-ene reaction
are known as highly reactive polyisobutylenes (HRPIBs) (Scheme 1a). In addition to manufacturing ashless dispersants [11], PIB-SAs have found application in the production of antifouling agents, detergents, and corrosion inhibitors [12].
London, UK), GLISSOPAL (BASF) RB HR PIB (RB Products, Inc., Houston, TX, USA), and others, with the use of BF3/ROH or BF3/H2O initiators [13,14,15]. Polymerization of isobutylene with a formation of HRPIB and PIB-SA (a); PIB with internal olefinic group and PIB-SA (b); and PIB-SA (c). Synthesis of bPIB-SI (d). It is important to note that the
synthesis of PIB-SA was previously based on the use of low-MW polyisobutylenes containing internal C=C fragments, obtained in the presence of AlCl3 or chloroalkylaluminum initiators. This approach included an additional stage of chlorination, followed by a Diels-Alder reaction of the diene intermediate with MA (Scheme 1b)
 [16,17,18]. This method currently seems less applicable due to ecological requirements; however, the same requirements necessary to dismiss the low-temperature controlled 'living' polymerization of IB initiated by tert-alkyl chlorides
(PhCMe2Cl and, later, tBuCH2CMe2Cl) with a formation of CMe2Cl-terminated PIBs [20] (Scheme 1c). According to the statistical data presented in a recent bibliographic review [21], the topic of IB polymerization is still relevant, and the focus is on the search for available, convenient, and "green" catalysts to produce HRPIB and reactive PIBs, and
their applications (Figure 1). The cationic polymerization of IB at ambient temperature was reviewed by Kostjuk et al. in 2013 [22]. In a more recent work [23], the chain transfer catalysts and initiators involving weakly
coordinating anions, such as perfluoroaryl borates and similar systems, attracted researchers' attention [15,24]; however, these approaches were not particularly effective in the synthesis of relatively low-MW HRPIB [25]. Nevertheless, the use of cationic initiators in combination with weakly coordinating anions remains present in the synthesis of
high-MW PIBs with exo-olefinic end-groups [26,27,28]. PIB-Cl can be transformed into HRPIBs via quenching with bases [29,30], but this method seems overly complicated and costly in comparison with BF3-based approaches applied to low-MW HRPIBs. The results of the reference search for "Reactive" AND "Polyisobutylene" (SciFinder, 15 June
2023). In a recent review [2], Kostjuk et al. have suggested that newly developed IB polymerization catalysts are complexes of metal halides with ethers; these complexes are poorly soluble in hydrocarbons. The latter disadvantage was overcome by the development of second-
generation catalysts, complexes of alkylaluminum dichlorides with ethers. The third-generation and PIB characterization, and analyze actual catalystic approaches to HRPIB in comparison with industrial industrial catalysts, are heterogeneous systems. In the present paper, we summarize and discuss the fundamental issues of the mechanisms of IB polymerization and PIB characterization, and analyze actual catalystic approaches to HRPIB in comparison with industrial catalysts.
catalysts. Our review is based on articles and patents published since 2010, and particular attention is given to recent articles not included in previous reviews. However, the negative trend visible in Figure 1 has nothing in common with the applications of HRPIBs and PIB-Cl. Recent studies of HRPIB and PIB-Cl functionalization, as well as
applications of the materials obtained, are also the subject of our review. The microstructure of the products of IB polymerization is an objective basis for the development of exo-olefinic groups. The Mn requirements of HRPIB (several kDa) greatly simplify
the chain-end analysis of the polymers using NMR spectroscopy; however, the possibility of chain scission processes occurring during IB polymerization requires the use of mass spectrometry for the analysis of PIB. The basic methods of the earlier
studies in our review with recent add-ons. The main types of unsaturated end-groups, related to the desired HRPIB structure and the products of the side processes, can be easily observed using 1H NMR spectroscopy [31]. As can be detected through the presence of singlets at \delta = 4.68 and the products of the side processes, can be easily observed using 1H NMR spectroscopy [31].
4.89 ppm; the singlet at 5.19 ppm corresponds to the endo-olefinic group. The presence of -CMe2Cl end-group distribution during ionization of PIB-Cl in hexanes. [PIB-Cl] = 0.015 M, [EtAlCl2] = 0.015 M, and [DTBP] =
0.015 M. The letters a, a indicate characteristic signals of >CH- fragments; the letters b, c, d and d refer to signals of olefin protons. Reprinted with permission from [31]. Copyright (2011) American Chemical Society. More detailed analysis of the 1H NMR spectra of PIB was carried out by Liu et al. on the product of IB polymerization initiated by
H2O/FeCl3 at 0 °C [32]. The structural types of the olefinic fragments and their assignment are presented in Figure 3. The strong resonance signals at \delta = 1.11 ppm (z) and 1.42 ppm (y) were assignment are presented in Figure 3. The structural types of the main chain of PIB, respectively; the signal of -C(CH3)3 head group was observed at \delta = 0.99 ppm. 1H NMR
spectrum of PIB obtained with the H2O/FeCl3 initiating system. The PIB sample comprises polymers with exo- (A) and endo-(B) olefinic end-groups (C, D), tetrasubstituted olefinic end-groups in 1H NMR spectra are indicated by corresponding
lowercase letters. Reprinted with permission from [32]. Copyright (2011) American Chemical Society. The \beta-proton abstraction from the growing tertiary carbocation normally leads to exo- or endo-olefinic end-groups, -CH2C(CH3)=CH2 (A, \delta = 4.64 and 4.85 ppm) or -CH2CH = C(CH3)2 (B, \delta = 5.15 ppm). The two strong quartet resonances at \delta =
5.17 and 5.37 ppm (c1, c2) and the intensive multiple resonances at \delta = 2.85 ppm (e) were attributed to -C(CH3)=CH(CH3) (C for Z- and E- configuration) and -CH2C(CH3)=CH(CH3) (C for Z- and E- configuration) and -CH2C(CH3) (C for Z- and E- configuration) a
\delta = 5.12 ppm was attributed to the vinyl proton in -C(CH3)=CHC(CH3)2 (D). In addition, many minor undefined resonances at \delta = 5.01, 5.03 and \delta = 5.06, 5.08 ppm, and triplet resonances at \delta = 5.30 ppm. The formation of F1 and F2 is a substantial side process during
the synthesis of HRPIB, and corresponding signals f1 and f2 at \delta = 4.82 and 4.80 ppm are more visible in the 1H NMR spectra of HRPIB (Figure 4) [33]. These signals can be attributed to the products of 1,3-methide migration (see Section 2.2) or to the protons of =CH2 in the coupled PIBs formed by the addition of a growing PIB carbenium ion to the
exo-olefinic end group in another PIB chain. To determine the real reaction pathway, NMR studies should be accompanied by size exclusion chromatography of PIBs (see Section 2.1.3). 1H NMR spectrum of PIB obtained with the AlCl3/OBu2/H2O initiating system. The PIB sample comprises polymers with exo- (A) or endo-(B) olefinic end-groups, and the AlCl3/OBu2/H2O initiating system.
internal vinylene isomers (F1, F2). The signals of the end-groups in 1H NMR spectra are indicated by corresponding lowercase letters. Reprinted with permission from [33]. Copyright (2010) Elsevier B. V.The 13C NMR spectra of PIB, prepared using H2O/FeCl3/iPrOH system [34], and
commercial GLISSOPAL 1000 are presented in Figure 5. 13C NMR spectra of HRPIB prepared from the mixed C4 fraction feed (top) and commercial HRPIB (GLISSOPAL 1000, bottom). Reprinted with permission from [34].
can be used for the determination of Mn. However, the presence of low-MW products of the chain scission can complicate the analysis of PIB spectra. Mechanistic causes of the formation of tri-substituted olefinic end-groups (see Section 2.2) have been determined using mass spectrometry: appearance of the odd-numbered peaks clearly indicated the
possibility of the chain scission during IB polymerization. Dimitrov et al. [31] have analyzed the samples of HRPIB (provided by Infenium) using atmospheric pressure photoionization time-of-flight mass spectrometry (APPI-TOF MS) and have found that only one series of peaks
appears in the APPI-TOF mass spectrum of HRPIB (Figure 6a). In APPI-TOF mass spectrum of "conventional" PIB, meanwhile, three additional series of peaks were observed with a mass difference of 14 Da, which corresponds to the -CH2- fragment (Figure 6b) [31]. (a) Negative-ion APPI-TOF mass spectrum of HRPIB sample from BASF; and (b)
negative-ion APPI-TOF mass spectrum of PIB sample from Infenium. Reprinted with permission from [31]. Copyright (2011) American Chemical Society. Size exclusion chromatography (SEC) is a separation technique which is widely used for the
polymers require calibration using polymer standards with known molecular masses and dispersities. However, in everyday practice, such standards are not readily available. Based on universal calibrating principle [35], the relationship between molecular weight M and intrinsic viscosity [η] is described using the Mark-Houwink Equation (1):
Reported values of K and \alpha value pairs for PIB were quite different. This issue was clarified by the studies of Puskas et al. [36] using PIB samples with Mv 1-1100 kDa. As a result of the measurements, the values K = 2.0 \cdot 10 - 4 dL·g-1 and \alpha = 0.67 have been obtained. In the follow-up work [37], Puskas et al. referred to the problems of the study of
branched PIBs, and proposed the use of hyphenated SEC techniques such as SEC coupled with multi-angle laser light scattering (VIS/RALS). As a result of this study, empirical Equation (2) was established.
 ML=Mw0.145+Mz-0.02-20.96, (2) where ML is Mooney viscosity, Mw is number average molar mass, and Mz is Z-average molar mass of the polymer. In a recent work [38], fractionations of commercial low-MW HRPIB (Mn = 880 Da and DM=5.1) were performed. "Conventional" PIB contained
more low-MW fraction (up to 200 Da), 4.8 vs. 1.3%, and high-MW fraction (>5 kDa), 28.8 vs. 2.4%. Combination of the fractions allowed to determine chain-end structures of macromolecules and propose the mechanisms of the formation of different unsaturated fragments. Isobutylene is capable of being
polymerized via cationic [20] and free-radical [39] mechanisms. Free-radical polymerization of IB was carried out previously using tBuN=NtBu initiator in the presence of LiCB11Me12 with a formation of IB, complexed with
cyclodextrin and dissolved in water. Linear PIBs with degree of polymerization (DPn) > 30 were obtained, and the method was proposed for the synthesis of block copolymers with acrylates. However, PIBs with -CH=CMe2 end-groups were formed during free-radical polymerization. In this way, it can be concluded that the controlled synthesis of
linear PIBs with highly reactive end-groups should be based on cationic species react with IB to yield cationic adducts. The chain propagation involves the repetitive addition of isobutylene to the growing carbenium ion until a chain release via chain
transfer to IB or other chain transfer agent occurs [23]. It is important to note that the formation of carbenium ions can be accelerated by the addition of Lewis bases; this phenomenon was first observed and explained by Penczek in 1992 [43]. At strong negative temperatures, IB polymerization proceeds as a "living" process, which opens the way for
obtaining HRPIBs or functionalized HRPIBs by quenching with different reagents [44]. At subzero and ambient temperatures, cationic polymerization of IB is often complicated by non-selective proton transfer to monomer or chain scission with a formation of
>C=C< fragments. The mechanism of IB polymerization was studied in detail more than 10 years ago by Dimitrov et al. [31] on the transformations of model PIB-Cl oligomers in the presence of EtAlCl2. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of the reaction product, obtained at 0 °C, contained two main
series of the peaks. The lower intensity series was identical with that of the starting PIB, while the more intense series was 14 Da (mass of one -CH2- group) higher and could only form by a loss of C4n-3 fragments. To prevent reprotonation, ionization of PIB-Cl by EtAlCl2 in the presence of 2,6-di-tert-butylpyridine (DTBP) was studied at different
temperatures using 1H NMR spectroscopy (see Section 2.1.1). In the presence of DTBP, exo- and endo-olefins were formed, and their amount increased with increasing temperature (Table 1). This suggests that the activation energy for proton elimination is higher than that for isomerization/chain scission. In the absence of DTBP, exo- and endo-olefins were formed, and their amount increased with increasing temperature (Table 1).
olefins were virtually absent at all temperatures, which can be attributed to a preference for reprotonation, subsequent isomerization, and chain scission. Tri-substituted olefins. Ionization of [PIB-Cl] = 0.015 M with [Et2AlCl] =
0.015 M in hydrocarbons for 30 min in the presence of [DTBP] = 0.015 M [31]. T, °C Olefin End-Group Distribution, % tri-Substituted exo- endo- tetra-Substituted exo- endo- endo- tetra-Substituted exo- endo- end
density functional theory (DFT) method (B3LYP/6-31G level of theory, Scheme 2) [31]. Upon ionization, the least stable tertiary cation 1 is formed. A 2-1 hydride shift to form 2 is energetically unfavorable but is not prohibitive. After formation of 2, the system compensates for the loss of energy by further rearrangement via a methyde shift leading to
3, which is the second most stable tertiary cation. As previously reported, the hydride transfer between carbocations 3 and 4 requires very little activation energy [45]. It should be noted that exo-olefin is more stable in comparison with endo-isomer, i.e., the proton transfer with a formation of exo-olefinic group is favorable both sterically and
thermodynamically. Interconversions and relative stability (E scale) of model cations and olefins based on isobutylene trimer [31]. To determine where the chain scission takes place, partially deuterated model polymers with the composition PhCMe2(IB-d8)13(IB)nCl (n = 1-6) were synthesized and subjected to ionization with EtAlCl2 at -40 °C in the
presence of DTBP. 1H NMR spectral studies showed that ~3-4 IB units are cleaved during the formation of tri-substituted olefins. Proposed mechanism of the cleavage was based on the assumption that type 4 carbenium ion may have undergone backbiting via a six-membered transition state [31]. Similar reaction pathway was proposed earlier for
degenerative 1,5-hydride shift in 2,6-dimethyl-2-heptyl cation (Figure 7); activation barrier for this process was estimated to be ~10 kcal•mol-1 (E scale, MP2/6-311G(d,p)-optimized geometries of the transition state (a) and the key intermediate (b) for degenerative 1,5-hydride shift in 2,6-dimethyl-2-heptyl cation
(B3LYP/6-311G(d,p) values in parentheses, and the values obtained via B3LYP/6-31G(d) SCI-PCM reaction field model are presented in bold). Reprinted with permission from [46]. Copyright (2006) American Chemical Society. In this way, the reaction mechanism of IB polymerization should be extended to include the chain scission (Scheme 3). In sum,
all side products can be correlated with type 3 and 4 cations; at sub-zero temperatures backbiting and chain scission during isobutylene polymerization [31]. Cation rearrangements and chain scission processes, discussed above, are
more actual for cationic IB polymerization, catalyzed by AlCl3/H2O and other conventional catalysts unsuitable for the synthesis of HRPIB. During the formation of "internal" exo-olefins during cationic polymerization of IB [33]. When using toluene as a solvent, for
some catalysts (e.g., iBuAlCl2) IB polymerization is complicated by alkylation of the solvent, which leads to the formation of very short PIB chains are terminated by a toluene. To clarify the reasons why only very short PIB chains are terminated by a toluene.
formed after protonation of IB (tBu+) and also after the addition of 1, 2, 3 and 5 IB molecules; the calculated values of natural bond orbital (NBO) charges were +0.538, +0.526, +0.514, +0.512 and +0.510, respectively [47]. Reducing the charge entails decrease in the reactivity; however, this effect disappears for DPn > 5, and cannot be used for the
chain control. In 2023, Lee et al. tried to create single-state and multi-state model with a chain transfer to proton was performed for AlCl3/H2O system at 0, 20 and 40 °C with
quite good results, despite the debatable assumption about two-stage process of the formation of initiating species (modern ideas about these species are discussed in Section 3.3). Another industrially important aspect of the chemistry of PIB cations is their reactivity towards other unsaturated hydrocarbons, especially C4 mixed hydrocarbon feeds
De and Faust showed that when using TiCl4 catalyst at 0 °C in n-hexane media, isobutylene is ~17 times more reactive than but-1-ene, and ~294 times more reactive than but-1-ene, and ~294 times more reactive than but-1-ene, and ~294 times more reactive than but-1-ene.
formed during capping reactions with C4 hydrocarbons (e. g. (Z)-but-2-ene formed -CHMeCHMeCl (~40%), -CMeClEt (~50%) and -CH2C(Me)=CH2 (~10%) end-fragments). Note that relative reactivities observed in the interaction of C4 olefins with the p-methoxy-
substituted diphenylmethyl cation in CH2Cl2 at -70 °C, reported earlier by Mayr [50]. In conclusion of this section, it is worth considering the process opposite to cationic polymerization, viz. enthalpy-driven PIB depolymerization. In the presence of CF3SO3H, HRPIB depolymerization in CH2Cl2 at -70 °C, reported earlier by Mayr [50]. In conclusion of this section, it is worth considering the process opposite to cationic polymerization.
presumably favored by the formation of stronger Csp2—Csp3 bonds in PIB [51]. This reaction is a particular case of reversible polymerization that has attracted the attention of researchers in recent years [52]; its importance for the synthesis of HRPIB is shaped by the understanding
that aromatic solvents can not only terminate cationic polymerization of IB, but also depolymerization should be carried out in bulk or in inert solvents (saturated hydrocarbons, MeCl, etc.). Current technologies of the production of PIBs and their practical applications were considered previously in a
number of reviews [1,3,53]. Butyl rubber [42] and halogenated butyl rubbers [1] occupy a significant share of the PIB market; however, the topic of copolymerization of IB with dienes and subsequent chemical modifications are beyond the subject of our review. From the mechanistic point of view and taking into account the catalysts used, the
controlled syntheses of low-MW HRPIBs, as well as medium- and high-MW PIBs, are of practical interest (Scheme 5). (Co)polymerization of IB and practically important products. Depending on the target MW values and chain-end structure, different catalytic systems and polymerization of IB and practically important products. Depending on the target MW values and chain-end structure, different catalytic systems and polymerization of IB and practically important products. Depending on the target MW values and chain-end structure, different catalytic systems and polymerization of IB and practically important products.
catalysts are successfully used for the production of low-MW HRPIBs [13,14,15], whereas AlCl3/ROH (or H2O) and related systems are used for the synthesis of medium-MW polymers [33]. High-MW PIBs dominated the market in 2023 in monetary terms [4], whereas low-MW HRPIBs continue to be the leading volume products, making the study of
new efficient catalysts for their synthesis much interesting. Although BF3/ROH catalysts have been used in bulk production of HRPIB in recent decades, further studies on the optimization of this system is still underway. Outstanding breakthroughs in this field seem unlikely; however, the results of actual studies in this field have been published. As
shown in [54], BF3/MeOH can be used as a catalyst for HRPIB production from the technical mixture of C4 hydrocarbons (45 wt% IB; the rest of the components were but-1-ene, but-2-enes and butanes). Polymerization at -20 °C using 0.5 wt% of the catalyst resulted in HRPIB with an Mn of ~1 kDa. Polymerization of C4 hydrocarbon mixtures
containing 36-46 wt% of IB using continuous-flow addition of the BF3/MeOH catalyst resulted in HRPIB with Mn = 0.93-1.23 kDa and an exo-olefin content of 71.2-82.3% [55]. Continuous-flow method was also applied for the production of low-MW HRPIB (C8-C28 mixture with 31 wt% of C16) [56]. Polymerization of IB, diluted with an equal amount
of butane, with the use of 0.25% BF3 and iPrOH (2:3 ratio) at -27 °C yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin content of 87.5%; at -17 °C HRPIB, it yielded HRPIB with lower Mn of 0.96 kDa and an exo-olefin
HRPIB. During polymerization of pure IB, continuous-flow addition of the catalyst resulted in increase in the exo-olefin content up to 88% [58]. To produce low-MW HRPIB, the use of IB dimer of the formula tBuCH2C(Me)=CH2 as a chain transfer agent and 2,6-di-tert-butyl-4-methylphenol as a polymerization-retarding agent were proposed in the
patent of the TPG Group [59]. Addition of polymerization-retarding agent resulted in a decrease in the ĐM values of PIBs. For BF3-catalyzed processes, IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the efforts to drive the reaction to higher IB conversions are typically 75-85%; however, all the reaction to higher IB conversions are typically 75-85%;
neutralizing the catalyst and using an impurity adsorption column for removing halogen acid from the distilled material [57]. In this way, monomer recycling implies irreversible consumption of the BF3-based catalyst and an accumulation of fluorine- and boron-containing wastewater that later need handling and treatment. Theoretical study of the
reaction of IB with BF3-H2O complex in n-heptane media was conducted recently by Babkin et al. [60] (ab initio, 6-311G** level of theory). They showed that the presence of n-heptane media was conducted recently by Babkin et al. [60] (ab initio, 6-311G** level of theory).
absence and in the presence of n-heptane (Me3C...FBF2(OH) and Me2CCH2H...O(H)BF3, respectively) raises reasonable questions about the reliability of the modeling. In 2019, mixed catalytic system comprising BF3/EtOH and TiCl4/H2O was studied by Liu et al. [61]. They detected a strong synergistic effect between catalyst components; PIBs with
Mn = 20-60 kDa were obtained. In conclusion of this section, successful heterogenization with the use of calcined (700 °C) mesoporous γ-Al2O3 or silica-aluminas, treated with BF3 or BF3/MeOH, respectively. In the first case, polymerization of 63 g of IB
using 0.4 g of the catalyst (-5 °C for 40 min) afforded HRPIB with (76% conversion, Mn = 900 Da, and exo-olefin content of 82%). When using silica-alumina/BF3/MeOH catalyst (0.2 g) in 45 g of IB polymerized at -5 °C within 20 min with a conversion of 91%, HRPIB with (Mn = 910 Da and exo-olefin content of 80%) was obtained. AlCl3-catalyzed
polymerization of IB produces conventional PIBs which contain up to 90% of internal double bond end-groups (trisubstituted and tetrasubstituted) [33]. However, since H2O can be used as an initiator for the first-generation AlCl3-based catalysts, the reaction of H2O with AlCl3 with the formation of catalytically active species is of particular interest
and worthy of separate consideration. The first molecular-level study of the acid-catalyzed IB polymerization was carried out by Johnson's group in 2018 on the H2O/AlCl3 system [63]. Generally accepted view on the nature of the catalytic species as AlCl3-OH2 was not confirmed with DFT calculations (BP86/def2-SVP level of theory; gas phase): the
formation of Al2 species of the formula Cl3Al(μ-OH)(μ-H)AlCl3 (Scheme 6) proved to be preferable. In particular, calculated Ea for the initiation of IB polymerization with AlCl3-OH2 was 21.6 kcal•mol-1. In contrast, the value of Ea for Cl3Al(μ-OH)(μ-H)AlCl3-initiated process was only 5.2 kcal•mol-1, and subsequent stages were found to be
exothermic (Figure 8). Summary of the proposed initiation and propagation mechanisms with Cl3Al(μ-OH)(μ-H)AlCl3 [63]. Potential energy surfaces for (a) IB initiation with permission from [63]. Copyright (2018) American Chemical
Society. Calculations of the solvent effect (CH2Cl2, conductor-like screening continuum solvation model) resulted in substantial decrease in the activation barriers (E2 = 3.2 kcal·mol-1 for initiation stage), indicating that Cl3Al(\mu-OH)(\mu-H)AlCl3 is likely to be an active catalyst in polar solvents at strongly negative temperatures. The reaction sequence
can be attributed to "living" IB polymerization. However, possible reaction pathways of chain release via proton transfer to monomer of elimination with a formation system for AlCl3-catalyzed polymerization of IB [64] resulted in obtaining PIBs with Mn
= 20-100 kDa; the content of exo-olefinic end-groups in the reaction products was low. In conclusion, it should be noted that AlCl3 (or HCl/Et2AlCl) was used as a catalyst for low-temperature IB copolymerization with polyfarnesene to obtain highly branched PIBs [65]. The nature of the end-groups was not considered in this patent. In the absence of
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Brønsted acids, initiation of IB polymerization usually requires the use of tert-alkyl chloride (cumyl chloride, tBuCH2CMe2Cl, tBuCl etc) as an initiator [66]. At the same time, in the first study of living IB polymerization, MeC(O)OCMe2Ph/BCl3 and related systems were used [67]. Commonly, the similar systems invariably consist of two components, namely an initiator (cationogen) and a coinitiator (Lewis acid); their development demonstrates that proper combination of IB. Among recent publications

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the study of Wu et al. [68] deserves a separate mention. They have demonstrated that 1,3-bis(1-chloro-1-methyethyl)benzene, a bifunctional initiator commonly used worldwide in carbocationic polymerization, in the case of IB can form indane derivative (Scheme 7a). To avoid this side process, 5-substituted derivative (Scheme 7b), similar to the one
previously suggested by Kennedy's group [69], was proposed. Living IB polymerization was terminated by buta-1,3-diene and MeOH with the formation of PIB-Cl containing highly reactive and easily hydrolyzable CH=CHCH2Cl end-fragments. (a) Mechanism of the formation of PIB-Cl containing highly reactive and easily hydrolyzable CH=CHCH2Cl end-fragments.
an initiator; and (b) mechanism of the synthesis of Cl-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-Allyl-PIB-A
catalytic systems is the ability to conduct IB polymerization at temperatures above zero Celsius with a retention of high exo-olefin content in the synthesis of HRPIBs, were the complexes of metal halides with ethers. In 2010, Kostjuk et al. proposed a
simple and prospective initiating system for the synthesis of HRPIB using cumyl alcohol and AlCl3/Bu2O [70]; similar type of the initiating system was reported independently by Wu et al. [33]. The most valuable finding of the study by Kostjuk et al. was the gradual decrease in IB conversion and MW of PIB when reaction temperature was increased
from -60 to -20 °C [70]. On the other hand, increasing the temperature did not significantly influence the content of exo-olefinic end-groups. High activities and regioselectivity were achieved in CH2Cl2 and toluene solvents, whereas a number of limitations (lower activity and exo-olefinic end-groups. High activities and regioselectivity were achieved in CH2Cl2 and toluene solvents, whereas a number of limitations (lower activity and exo-olefinic end-groups. High activities and regioselectivity were achieved in CH2Cl2 and toluene solvents, whereas a number of limitations (lower activity and exo-olefinic end-groups.)
media [71]. In [33], Wu et al. have clearly demonstrated the marked difference in catalytic systems. As can be seen in Figure 9, when using AlCl3/H2O and AlCl3/H2O and AlCl3/H2O or products. 1H NMR spectrum (300 MHz) of
PIB obtained with the AlCl3/H2O initiating system. Conditions: [AlCl3] = 0.002 M; [IB] = 1.82 M; [H2O] = 0.0007 M; CH2Cl2; T = 0 °C; t = 20 min. The PIB sample comprises polymers with exo-olefinic end-groups in 1H NMR spectra
are indicated by corresponding lowercase letters. Reprinted with permission from [33]. Copyright (2010) Elsevier B. V.For AlCl3/Bu2O catalytic system with H2O as an initiator, exo-olefinic fragments have proven to be the major end-groups [33]. Apparently, weakly coordinating anion [Bu2O...AlCl3(OH)] – promotes the rapid β-proton abstraction from
 -CH3 of the growing chain-ends with the formation of exo-olefinic end-groups and decreases the carbenium ion rearrangements. In addition, the small amount of excess Bu2O probably could act as a Lewis base to suppress isomerization. For the AlCl3/iPr2O system, similar results were reported; the main signals in 1H NMR spectrum corresponded to
the signals of exo-olefinic end-groups (Figure 4). When using the AlCl3/Bu2O catalytic system, at 0 °C HRPIBs with an Mn of 1.5-3.3 kDa and an exo-olefin content decreased). At 20 °C and 45% IB conversion, the exo-olefin content was
82%. Faust et al. [72] have proven that cumyl alcohol is not a true initiator in conjunction with the AlCl3/R2O catalytic system (this conclusion was drawn based on results of polymerization experiments in the presence of DTP that showed zero activity); the process is initiated with water. Mechanistic studies suggested that the reaction of water with
AlCl3 R2O yields H+[AlCl3OH]-, which initiates the polymerization, and free R2O, which abstracts β-proton. In other words, the role of the AlCl3 R2O complex is to deliver R2O molecules to close proximity of the propagating PIB end. In [71], Kostjuk et al. showed that the initiation with water is preferable; when using AlCl3 Bu2O/H2O, PIBs with 89 and 100 are the complex is to deliver R2O molecules to close proximity of the propagating PIB end. In [71], Kostjuk et al. showed that the initiation with water is preferable; when using AlCl3 Bu2O/H2O, PIBs with 89 are the complex is to deliver R2O molecules to close proximity of the propagating PIB end. In [71], Kostjuk et al. showed that the initiation with water is preferable; when using AlCl3 Bu2O/H2O, PIBs with 89 are the complex is to deliver R2O molecules to close proximity of the propagating PIB end. In [71], Kostjuk et al. showed that the initiation with water is preferable; when using AlCl3 Bu2O/H2O, PIBs with 89 are the complex is the comple
94\% content of exo-olefinic end-groups were obtained in high yield (>85%) within 10 min; Mn of PIBs obtained was controlled in a range of 1-10 kDa by changing the reaction temperature from -40 to 30 °C. During the study of IB polymerization, co-initiation by AlCl3 complexes with different linear (Et2O, Bu2O, Am2O, Hex2O, MeOPh) and branched
(iPr2O, tBuOMe) ethers in toluene or CH2Cl2 at 20 °C was investigated [73]; the complexes with ethers of moderate basicity (AlCl3•Bu2O and AlCl3•iPr2O) afforded PIBs with the highest exo-olefin content (80-95%) and IB conversion, while the use of PhOMe led to the conventional PIBs containing mainly tri- and tetra-substituted olefinic end-groups.
The complexes of AlCl3 with tBuOMe and THF were inactive due to the ether cleavage by AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the presence of AlCl3. The polymerization of IB in the polymerization of IB in the presence of AlCl3. The polymerization of IB in 
containing 70-85% exo-olefinic terminal groups [73]. The 1:1 complexes of AlCl3 with linear ethers were found to be stable and more exchangeable complexes was detected. It is noteworthy that both polymerization rate and chain-end structure of
PIB were vulnerable to AlCl3/ether ratio: as can be seen in Figure 10, at the ether-starved conditions (AlCl3/Bu2O = 1:1.2) resulted in a
 significant decrease in the reaction rate and exo-olefin content, and endo-olefin was the main side product. Another significant result reported in [73] was the control of Mn of PIB within the limits of 3-8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the length of R in AlCl3 \cdot 8 kDa by the l
in toluene at different AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. Alcl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. Alcl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. Alcl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. Alcl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. Alcl3/Bu2O ratios: [co-init
In both solvents, AlCl3•iPr2O showed higher exo-olefin content than AlCl3•Bu2O; the presence of small excess of iPr2O over AlCl3 (5-10 mol%) resulted in an increase in vinylidene selectivity in some cases. The marked difference between toluene and n-hexane was in the effect of temperature on the exo-olefin content,
which increased in toluene and decreased in n-hexane as the temperature window was extended from −20 to 50 °C, and the Mn was adjustable between 0.5 and 15 kDa. However, exo-olefin content in
the reaction products of the first experiments was 76% or less. Optimization of the reaction conditions in CH2Cl2 was successful: at 20 °C the selectivity of 89% was achieved with 63% conversion of IB (Mn = 1.29 kDa, ĐM = 1.7); the excess of iPr2O over AlCl3 was necessary to avoid the existence of free AlCl3 [75]. In further studies of the
AlCl3•iPr2O system [76], the effect of ethyl benzoate (EB) was evaluated. The reactions at -30 °C were also conducted in a microflow reactor, and PIBS with Mn = 14.3-47.5 kDa and an exo-olefin content of 29-76\% were obtained. In more recent works, some aspects of the interactions in AlCl3/R2O/H2O system were detailed [77]. The value of these
results for the synthesis of commercially demanded HRPIBs seems questionable. The use of AlCl3•iPr2O as a co-initiator of the polymerization of C4 hydrocarbon feed was studied by Kostjuk et al. [78]. The reaction proceeded at a considerably lower rate in comparison with the polymerization of pure IB yielding PIBs with higher Mn and exo-olefinic
end-group content. At 0 °C, Mn was 4.37 kDa, that is too high value in comparison with Mn required for practical applications of low-MW HRPIBs (<2.3 kDa) [12]. Two-component catalytic system, based on AlCl3•iPr2O and AlCl3
component that stabilized carbenium ions, and the function of AlCl3•Et2O was to promote proton elimination. Polymerizations were conducted in a microflow system with [IB] = 0.33-1.30 M in the presence of H2O as an initiator. The yields of IBs were up to 89% after 10 min, and the exo-olefin group content was 60-75%. In recent patents [80,81], the
results of the study of AlCl3/R2O catalyst in IB polymerization (4 M in hexanes) at 0 °C have been presented. As can be seen in Table 2, the use of ether mixtures allowed to optimize the process (Table 2, Entry 8); the replacement of the
solvent with toluene, as well as Bu2O with THF, had no effect. Polymerization of IB using AlCl3/R2O catalysts at 0 °C. [IB] = 4 M in hexane; reaction time 1 h [80,81]. Entry [AlCl3], M [iPr2O], M [Bu2O], M Conv., % 1 Mn, kDa 2 exo-, % 1 0.01 0.01 - 98 1.3 56 2 0.01 - 0.01 28 2.8 77 3 0.01 0.005 0.005 98 1.5 78 4 0.01 0.0025 0.0075 97 1.5 66 5 0.01
0.0075 0.0025 62 2.1 79 6 0.01 0.001 0.009 30 2.8 76 7 0.01 0.009 0.001 98 1.4 58 8 0.01 0.006 0.006 98 1.0 84 9 0.01 0.005 0.005 98 1.4 77 13 4 0.01 0.005 0.005 95 1.5 79 The further increase in the polymerization temperature to 30 °C for AlCl3/R2O
systems (activated with water in 1:1 [Al]/[H2O] ratio) resulted in substantial loss of the formation of exo-olefinic groups (12-37%) [82]. The AlCl3-phenetole/TiCl4-H2O system was studied by Liu et al. [83]. They found that mixed catalyst exhibited activities 1.2-3 times higher than those for AlCl3/phenetole, and more than an order of the formation of exo-olefinic groups (12-37%) [82].
magnitude higher than those for TiCl4/H2O, which indicated a notable synergistic effect. However, relatively high-MW PIBs were obtained, and chain-end analysis was not conducted in this work. The results of the study by Deng et al. [84], that describes catalytic experiments with C4 mixed hydrocarbon feed, AlCl3/toluene and additional donors
(Et2O and ethyl acetate), are difficult to analyze because of the absence of data on chain-end structures of relatively low-MW PIBs obtained. In conclusion of this section, it is appropriate to mention the recent work of the chemists from Beijing University [85] who studied IB polymerization using the AlCl3/Bu2O catalytic system in a rotating packed
bed reactor. The effects of operating parameters including polymerization temperature (T), rotating speed (N) and relative dosage of the monomers and initiating systems ([M]0/[I]0 = 49) HRPIB with Mn = 2.55 \text{ kDa} and an exo-olefin content of 85\% was
obtained. The discovery of AlCl3/R2O catalytic system encouraged the intensive investigations of Et2O, Bu2O and iPr2O) in water-initiated polymerization of IB [32]. In the absence of ethers, conventional non-reactive PIB
was formed (see Figure 3 in Section 2.1). Among three ethers, iPr2O demonstrated the highest activity, and the maximum exo-olefin content (up to 90% at 0 °C) was observed when using Et2O. An increase in polymerization rate and an increase in vinylidene selectivity, which generally confirms the
possible role of R2O in β-proton abstraction proposed by Faust [72]. Up to 85% exo-olefin content was achieved in IB polymerization when using MCl3•iPr2O (M = Fe, Ga) complexes and tBuCl or tBuCH2CMe2Cl initiators [86]. Di-n-alkyl ethers did not form catalytically active complexes. Also of interest was the inertness of AlCl3•iPr2O analog in the
 ionization of tBuCH2CMe2Cl. Proposed reaction mechanism is presented in Scheme 8; tBuCH2CMe2Cl is ionized by Lewis acid/R2O complex to yield tBuCH2CMe2+, which initiates IB polymerization, and this ultimately results in the release of R2O from the complex. The propagating PIB+ may undergo proton elimination to yield PIB exo-olefin or
may be deactivated by ion collapse to yield PIB-Cl, which can be reactivated by Lewis acid. The abstracted proton may then start a new polymer chain after addition to the IB molecule. More detailed kinetic studies of the tBuCl/FeCl3•iPr2O system [87] only confirmed the results of the prior research [86], which is that the use of EtOCH2CH2Cl and
O(CH2CH2Cl)2 instead of iPr2O resulted in a decrease in catalytic activity and exo-selectivity. Possible mechanism for the polymerization of IB with the use of MCl3•R2O (M = Fe, Ga) and tBuCH2CMe2Cl [86]. In 2013, Faust et al. reported the results of a comparative study on the complexation of FeCl3 with different ethers and catalytic behavior of
the adducts in tBuCl-initiated IB polymerization [88]. At 0 °C in n-hexane ([IB] = 1.0 M, [tBuCl] = 0.02 M.), 81% conversion and 78% exo-selectivity were achieved after 20 min for R = iPr. However, all experiments with FeCl3•R2O in aliphatic media failed to achieve >80% content of exo-PIB. The role of the ether molecule in IB
polymerization was substantially clarified during the studies of living IB polymerization, initiated by tBuCH2CMe2Cl/TiCl4 and terminated by tBuCH2CMe2Cl/TiCl4 and terminated by tPr2O or sBu2O with a formation of exo-olefinic end-groups after treatment with MeOH [44]. In this study, the formation of PIB-OiPr2+ ions was proven using 1H NMR spectroscopy at -70 °C (Figure 11).
When branched ethers were used, 100% exo-selectivity was observed; however, experiments with tBuOMe, Bu2O and Et2O resulted in the formation of PIBs with 88, 82 and 69% of vinylidene PIB, respectively. 500 MHz 1H NMR spectrum of tBuCH2CMe2Cl/iPr2O oxonium ion adduct in the presence of 10 eq of TiCl4 in 50/50 (v/v) CS2/CD2Cl2 at -70
°C. The lines designated with "a-e" relate to fragments of reactive complex with the relevant designations; lines designated with permission from [44]. Copyright (2013) American Chemical Society. The possibility of direct synthesis of HRPIB on a
H2O/TiCl4/alcohol initiating system was studied by Wu et al. [89]. IB solution in n-hexane and mixed C4 fraction feed ([IB] = 2.9 M) were used in polymerization of IB from the mixed C4 fractions, resulting in the formation of HRPIBs with Mn
= 1.2-1.6 kDa and ĐM = 1.5-1.9; vinylidene selectivity was 80%. A possible reaction mechanism (Scheme 9) included the reaction between ROH and TiCl4 with the formation of TiCl3(OR) and HCl. In the presence of TiCl4, protic initiator H[Ti2Cl9-n(OR)n] (n = 0-2) formed and reacted with IB leading to tert-butyl cation and PIB. Fast initiation from
HCl resulted in higher monomer conversion, lower molecular weight, and narrower MWD of PIBs at higher concentration of ROH. The counter-anion [Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from -CH3 groups in the growing PIB chain-ends, and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends, and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the selective β-proton elimination from the growing PIB chain-ends and H[Ti2Cl9-n(OR)n] – affected the growing PIB chain-
HRPIB via cationic polymerization of isobutylene with H2O/TiCl4/ROH (iPrOH or iAmOH) initiating system [89]. When using water as an initiator, this catalyst have demonstrated higher exo-selectivity in non-polar solvents, which is distinct from AlCl3/R2O
systems. Recently, Kostjuk et al. have studied cationic polymerization of IB with dicumyl chloride/FeCl3/iPrOH in CH2Cl2/n-hexane 40/60 at -80 °C. They showed that this initiating system afforded bifunctional low-MW PIBs (Mn 1.25-21 kDa, ĐM \le 1.28) with -CMe2Cl end-groups that can be converted to HRPIBs by end quenching with iPr2O [90].
 When studying the catalytic properties of EtAlCl2 in combination with Et2O, EtOCH2CH2Cl)2 is an efficient donor component [91]. At 1:1 [Al]/[ether] ratio and 0 °C, exo-olefin content in PIB was 70%, but its value was increased to 90%
with the introduction of additional amounts of O(CH2CH2Cl)2 into the reaction. The calculated binding energies of ethers with EtAlCl2 (DFT, B3LYP/6-31G* level of theory) were -7.5, -7.1 and -5.1 kcal•mol-1 for Et2O, EtOCH2CH2Cl)2, respectively, which correlates with the ability of EtAlCl2 etherate to the displacement with
tBuCl with subsequent ionization and polymerization. Depending on the reaction temperature (from -20 to 10 °C), HRPIBs with an Mn of 1-4.5 kDa were obtained. Another study [92] was focused on the experimental procedure and have only demonstrated the importance of all experimental parameters, including the material of the reaction vessels:
when chrome stainless steel reactor was used, exo-selectivity of IB polymerization decreased from 90 to ~70%. In the studies of the kinetics and mechanism of IB polymerization, initiated by EtAlCl2·O(CH2CH2Cl)2 in hexanes at 0 °C, Faust et al. explained the first-order kinetic dependence on [IB] concentration and
independence of the reaction rate on [EtAlCl2]/[O(CH2CH2Cl)2] ratio by postulating an equilibrium between dormant oxonium and active carbenium ions [93]. An increase in the polymerization rate in the presence of water was explained in this work by the influence of water on oxonium/carbenium ions [93]. An increase in the polymerization rate in the presence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this work by the influence of water was explained in this way in the water was explained in this way in the influence of water was explained in this way in the water was explained in this way in the water was explained in this way in the water was explained in the water was explain
reaction mixture on IB polymerization (Scheme 10) was studied in [94]. In this work, it was shown that low levels of some organic impurities retard the polymerization of IB initiated by tBuCl and catalyzed by EtAlCl2/O(CH2CH2Cl)2 in hexanes at 0 °C. For efficient synthesis of HRPIB, the impurity scavenger Lewis acid needs to be insoluble in
hexanes and should not polymerize IB; FeCl3 was found to be efficient scavenger. Suggested modified mechanism of IB polymerization in the presence of impurities. Reprinted with permission from [94]. Copyright (2017) Wiley-VCH Verlag GmbH & Co.The EtAlCl2/O(CH2CH2Cl)2 initiating system was further optimized by using micromixing module
in the polymerization system [95]. HRPIBs with a 100% conversion were obtained within 5 min in the micromixing enhanced system at 20 °C, in comparison to only 30% conversion after 10 min in a conventional reactor. The Mn and exo-olefin content of HRPIBs were adjusted conveniently to the ratio of EtAlCl2 to O(CH2CH2Cl)2 and monomer
concentration. As a result, HRPIBs with Mn = 0.8-2.4 kDa, ĐM = 2.15-2.85 and exo-olefin content of 63-94% were obtained. Further studies on the EtAlCl2/O(CH2CH2Cl)2 initiating system at elevated temperature with minimal loss of the exo-olefin
content [96]. The increase in the polymerization rate was attributed to the increased steady state concentration of carbenium ions; polymerization selectivity depended on the stability of the corresponding tert-alkyloxonium shows that the oxonium ion is stable up
to 15 °C, and slowly decomposes at 20 °C (~15% after 6 min) with the formation of ethylene, isobutane and AlCl3 (Scheme 11). This process was clearly confirmed with 1H NMR spectroscopy. Formation of ethylene, isobutane and AlCl3 (Scheme 11).
use of C4 hydrocarbon feed instead of pure IB is highly attractive. Faust et al. studied the polymerization of IB in the presence of other C4 olefins, but-1-ene, cis-but-2-ene, and buta-1,3-diene using the tBuCl/EtAlCl2/O(CH2CH2Cl)2 initiating system in hexanes at 0 °C [97]. As shown in Figure 12, butenes were only marginally involved in
copolymerization with IB; buta-1,3-diene was more active, but its involvement was negligible due to its low content in the C4 feed. Involvement of C4 unsaturated hydrocarbons in IB polymerization, initiated by tBuCl/EtAlCl2/O(CH2CH2Cl)2. Reprinted with permission from [97]. Copyright (2017) American Chemical Society.IB polymerization using
H2O and RAlCl2•niPr2O (R = Me, Et, iBu; n = 0.6-1) in n-hexane at 10 °C was studied by Kostjuk et al. in 2014 [98]. EtAlCl2•niPr2O and iBuAlCl2•niPr2O and iBuAlCl2•niPr2O and iBuAlCl2•niPr2O (n = 0.8-0.9) afforded PIBs with Mn = 1-1.5 kDa and an exo-olefin content of 85-95%. To increase IB conversion and polymerization rate, a "delayed proton abstraction" approach was proposed.
i.e., co-initiation by RAICl2 and separately added ether. The most plausible mechanism of the reaction comprised the formation of alumoxanes. The activating effect of water was studied separately [99], and the best results were achieved when iBuAlCl2•0.8iPr2O reacted with a suspension of water in n-hexane before IB addition. These studies were
continued [100], and the conditions of the IB polymerization were optimized by pre-activation of iBuAlCl2 using wet argon or MgSO4•7H2O in the presence of iPr2O. The highest regioselectivity of polymerization was observed at the ratio [iBuAlCl2]/[iPr2O] of 0.4. The better control of DM was achieved by using a mixture of iPr2O and Et2O as an
additive. The optimized conditions were [IB] = 5.8 \, \text{M}, [iBuAlCl2 preact.] = 38 \, \text{mM}, [Et2O] = [1.20] = 7.6 \, \text{mM}, [E
and mixtures of the ethers was protected by the recent patent [101] (BASF). In [47], Kostjuk et al. reported on the use of H2O/iBu2AlCl and H2O/iBu2AlCl system initiated slow IB polymerization with a formation of high-MW PIB
(up to Mn = 55 kDa) with a DM of ~2.5 and an exo-olefin content of >85%. Addition of the ethers, iBuAlCl2 catalyzed the formation of ill-defined PIBs and alkylation of toluene (reaction solvent). The addition of the ethers made it possible to
control the polymerization; a decrease in R2O/iBuAlCl2 ratio resulted in an increase in IB conversion and Mn of PIB, and decreased the vinylidene selectivity. In the recent theoretical work of Zaikov et al. [102], qualitatively different view on the initiation of polymerization of IB with the use of Et2AlCl/ROH (R = H, Ph) was proposed. The authors
assumed that initiation of the IB molecule proceeds involving EtCl2Al...O(R)H species, and estimated the activation energies of this process at ab initio HF/3-21G level of theory. Regardless of the modeling results, the very idea of the hydrolytic stability of EtAlCl2 is doubtful. Addition of (Octyl)3Al to EtAlCl2/O(CH2CH2Cl)2 system resulted in a
decrease in the activity with a substantial increase in the exo-olefin functionality [103]. Initiation of IB polymerization using this system required tBuCl or traces the of water; in the latter case, an exo-olefin content of 81% was reached [104]. Promising results were obtained when using AlCl3/EtAlCl2 mixtures [80,81]. As can be seen in Table 3, the
low-MW HRPIB with an exo-olefin content of more than 80% was formed with high IP conversion in a number of experiments, still needs further explanation. Polymerization of IB using AlCl3 and/or EtAlCl2/R2O catalysts at 0 °C. [IB] = 4 M in hexane; reaction time 1 h
[80,81]. Entry [AlCl3], M [EtAlCl2], M [iPr20], M [iPr20], M [Bu20], M Conv., % 1 Mn, kDa 2 exo-, % 1 0.01 - 0.01 - 98 1.3 56 2 - 0.01 0.01 - 98 1.4 64 6 0.001 0.009 0.01 - 10 3.8 83 7 0.009 0.001 0.01 - 98 1.3 55 8 0.01 0.01 0.02 - 98 1.0 81 9 0.0025 0.0025 0.0025 0.005
70.2.8~80~10~0.01 - -0.01~28~2.8~77~11 - 0.01~28~2.8~77~11 - 0.01~99\% of the bisphenol A (BPA) was extracted phenols (200-500 mg·L-1) were also extracted with >95\% efficiency. Recycling of the PB-imidazole/PAO phase containing sequestered phenol
was easily performed by subsequent mixing with solid NaOH. These results are of great importance due to the high toxicity of BPA, which is widely used in the production of polycarbonates [157,158]. In 2021, Bergbreiter et al. proposed the use of fully recyclable PAO and soluble PAO-anchored PIB-bound sulfonic acid catalysts [159]. HRPIB with Mn
 = 432 was subjected to a thiol-ene reaction followed by oxidation affording PIB-SO3H with a 47% yield (Scheme 21). PIB analog of arenesulfonic acids, PIB-ArSO3H, was synthesized in two stages in a 62% yield via alkylation of anisole, followed by sulfonation (Scheme 21). Catalytic potential of sulfonic acids was studied during the reaction of
PhCH2OH with 3,4-dihydro-2H-pyran (5 mol% of the catalysts and >90% yields over 10 cycles); comparison showed that the p-dodecylbenzenesulfonic acid/PAO system lost activity after the third cycle. Catalytic potentials of PIB-SO3H and PIB-ArSO3H were also estimated for esterification and three-component condensation between PhCOH, urea
and acetoacetic ester; at least 80% yields of the products were achieved after recycling seven times and more [159]. Synthesis of PIB-bound (a) alkane and (b) arenesulfonic acids [159]. It is worth pointing out here that alkylation of the active aromatic compounds (substituted anilines) by HRPIB (Mn = 1 kDa) was efficiently used in the synthesis of
lipophilic azo dyes [160] (Scheme 22), that are the colored probes used in the study of high-boiling non-toxic solvents, including PAOs. Alkylation of 6-phenoxyhexan-1-amine by PIB-Cl resulted in an amino-functionalized PIB that was used for the stabilization of nanocrystalline semiconductors (CdSe and PbS) [161]. Synthesis of PIB-bound azo dyes
[160].PIB-substituted phenols were synthesized using alkylation of phenol by HRPIBs, and catalyzed by PhOH•BF3 in n-hexane/toluene media [162]. The structure of the reaction products is not entirely clear; 1H NMR data, presented in this patent, raise questions about the assignment of the signals. On the other hand, in [163], the structure of the
alkylation product was clearly proven. In this work, bifunctional HRPIB and the product of its reaction with phenol were used as starting compounds for the synthesis of PIBs with oxirane functionality; the reactions on one chain-end fragment are presented in Scheme 23. Alkylation of phenol by three-arm star HRPIB (prepared using 1,3,5-
glycidyl ether; (c) PIB exo-olefin epoxide; and (d) PIB cyclohexene epoxide [163] (mCPBA—3-chloroperbenzoic acid). In 2021 [165], Pebriani et al. published a controversial report on the synthesis of diamine derivatives of PIB based on direct acid-catalyzed interaction between HRPIB and pentaethylenehexamine. The structure of the reaction product
(Scheme 24), proposed by the authors, was confirmed via FT-IR spectra. In the absence of NMR data, this structure (as a result of nucleophilic addition to =CH2) raises reasonable doubts from a mechanistic point of view. Note that in another study [166], this process was called 'electrophilic substitution' (no NMR data). Some doubt is also expressed
regarding the choice of the solvent (o-xylene) that can react with HRPIB. BF3-catalyzed reaction of HRPIB with pentaethylenehexamine [165]. High reactivity of exo-olefin- and -CMe2Cl-terminated PIBs have been successfully used for the synthesis of amphiphilic block copolymers with excellent prospects for biomedical application and materials'
design [167]. In this section, we provide some practical examples of the preparation and applications of PIB copolymers (see Scheme 7) were hydrolyzed to the corresponding diols using aqueous tetrabutylammonium hydroxide in THF (reflux, 22 h, and 98.2% conversion); these diols in a mixture with
butane-1,4-diol were further used for polyuerthane preparation through the reaction with 4,4'-methylenebis(phenyl isocyanate) in the presence of Sn(Oct)2 [68]. In subsequent studies [168], the synthesis of a copolymer was optimized to achieve mechanical characteristics and biocompatibility suitable for a fully synthetic heart valve. With the use of
freshly distilled 4,4'-methylenebis(phenyl isocyanate) and increased MW (>100 kDa), a tensile strength of \approx32 MPa, an elongation of \approx630%, and a toughness of >4.0 J was achieved. This material had an impressive fatigue life, >1 million cycles around 1 MPa SED and
>0.5 million at 2-3 MPa SED; it exhibited no calcification, and had less protein adsorption and cell attachment in comparison with silicone-rubber materials. A similar copolymer, synthesized from (4-HOC6H4)-PIB-(4-C6H4OH), was proposed for medical applications in a recent patent of Medtronics Inc. [169]. Ring-opening polymerization-induced self-
assembly (ROPISA) was achieved by employing PIB-OH, diphenyl phosphate, cyclohexane, and ε-caprolactone (ε-CL) and/or δ-valerolactone (ε-CL) and/or δ-valerolactone (σ-VL). ROP at 80 °C interfered with the crystallization and in situ fixation, which readily reorganized nanoparticles and formed spherical micelles or precipitate. However, at 20 °C, fibrillar nanoparticles were
gradually formed and stabilized according to the classical polymerization-induced self-assembly (PISA) mechanism [170]. PIB-OH was also used as a starting compound for the synthesis of chain transfer agent PIB-OC(O)CH2CH2C(Me)(CN)SC(S)SC12H25 for reversible addition-fragmentation chain transfer (RAFT) polymerization of fatty ester
methacrylates [171]. The block copolymers showed varied crystalline behavior depending on the chain length of the fatty acids. PIB-Br-initiated alternating RAFT polymerization was also used in the synthesis of the copolymer of tert-butoxy carbonyl (Boc)-leucine containing a maleimide unit and Boc-alanine containing a styrene unit. Its deprotection
resulted in an amphiphilic copolymer with free -NH3+ and -COO- functionalities in an alternating fashion that demonstrated pH-responsive self-assembly [172]. A similar approach was used in the synthesis of PIB block copolymers containing aninonic (acrylic acid monomer), neutral (MeO(CH2CH2O)4-actylate monomer) and cationic ((Boc)-leucine-
OCH2CH2O-acrylate monomer) fragments, designed for ion transport through the liposomal membrane [173]. RAFT copolymerization was also used for the synthesis of PIB-containing copolymer with glucose-decorated hydrophilic segment that showed high efficiency in the protection of the insulin aggregation [174]. The prospects of using PIB blocks
in the design of stretchable semiconducting polymers was demonstrated on the example of ABA-type architecture comprising PIB and poly(naphthalenediimide-bithiophene) with a formation of 1:1 adducts and relatively high-MW polymers
[176]. The optimal molar ratio of PIB-SA to polyglycerol was found to be 1:1. Commercial HRPIB derivatives of the formula (PIB)CH2CH(Me)CH2CH2NH2 [177] were acylated with (meth)acrylates (tert-butyl-peroxyethylhexanoate as an initiator, tert-dodecyl mercaptan as a transfer
agent, at 95 °C, and with isoparaffin as a solvent) [178]. Similar methacrylic monomers were prepared via acylation of PIB-substituted phenols [162,179]. Resulting comb copolymers were proposed as viscosity index improvers for replacing
commercially used BF3 in the synthesis of HRPIBs is still relevant. Since 2010, a number of alternative catalytic systems have been studied. The most prospective initiators of the IB polymerization for the production of HRPIBs are the complexes of metal chlorides with ethers, the complexes of alkylmetal chlorides with ethers, and heterogeneous
catalytic complexes in aliphatic media should be solved. Further improvement in similar catalysts in terms of the selectivity of β-H elimination (preferably in n-hexane or in C4 feed), via both the design of new Lewis acids and new electron donors, can be complicated by the formation of relatively high-MW PIBs when highly active catalyst could be
found [22]. Also note that aromatic solvents are still proposed to be used in IB polymerization [80,81,84,126], even though aromatic hydrocarbons can undergo alkylation [47] and depolymerize PIBs in the presence of acids [51]. Using C4 hydrocarbons can undergo alkylation [47] and depolymerize PIBs in the presence of acids [51].
Therefore, new-generation catalysts should be active in a non-polar reaction medium and inert towards but-1-ene and but-2-enes, that hardly fits with a high catalytic activity in cationic processes. The first results in this field have already been published [34,78,84,89,97], but further studies are required on the use of hydrocarbon mixtures with
comprehensive analyses of the microstructure of polymers. In the development of heterogeneous catalysts for the production of HRPIBs, certain analogies with the development of supported α-olefin polymer particle morphology (irrelevant for more soluble PIBs), the problems
associated with the efficient and stable supporting of the active species, maximizing the surface area, and selecting the donor additives seem common for both processes. These problems have been solved successfully for Ziegler-Natta catalysts, and we can also expect this progress in the area of heterogeneous catalysis for IB cationic polymerization
in the near future. Finally, one cannot fail to note the structural similarity of HRPIBs and methylenealkanes, including vinylidene dimers and oligomers of α-olefins [180,181]. Apparently, the methods of HRPIBs and methylenealkanes, including vinylidene dimers and oligomers of α-olefins [180,181].
recently in catalytic transformations of methylenealkanes [182,183,184,185,186,187]. Conceptualization, I.E.N.; writing—original draft preparation, I.E.N.; writing—review and
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