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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→Polyisobutylene succinic anhydride (PIBSA) Properties: Appearance: Polyisobutylene succinic 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 production. Solubility: Generally soluble in hydrocarbons and chlorinated solvents. 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 lubricant. It enhances the dispersibility of contaminants such as dirt, soot, and metal particles in engine oils, contributing to cleaner engines and prolonged equipment life. Fuel Additive:In fuel formulations, PIBSA functions as a dispersant and detergent to maintain engine cleanliness, improve fuel efficiency, and reduce emissions. It helps prevent the formation of deposits in fuel injectors, carburetors, 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 corrosive agents. Other Applications:Adhesives and sealants Paints 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: Helps maintain cleanliness in engines and equipment by preventing the formation of deposits and sludge. Environmental Impact: Contributes to reducing emissions and extending 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. PIBSA1000 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 dispersion. Used for preparation of polyisobutylene diene and polyene succinimide and bononize ashless 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: PIBSI is formed by the reaction of PIBSA 1000 with a diamine. This reaction replaces the succinic anhydride groups on PIBSA with imide groups linked to the diamine molecule. Applications 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 power: Effectively keeps contaminants suspended in the oil, preventing deposit formation. Shear stability: Maintains its dispersing ability even under high shearing forces within the engine. Compatibility: Compatible with various base oils and other lubricant additives. Ashless formulation: Reduces the formation of ash deposits in the engine, contributing to cleaner emissions. Important Considerations: PIBSA 1000 itself is not directly added to lubricants. The selection of the appropriate ashless dispersant based on PIBSI (derived from PIBSA 1000) depends on various factors like:The type of lubricant Desired performance characteristics Compatibility with other 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 products with nearly 20 years of experience. Such as detergent、ashless dispersant、ZDDP、EP antiwear 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 offerings and may assist in selecting the most suitable ashless dispersant for your lubricant application. Product Introduction Polyisobutylene Succinic Anhydride is a lubricant additive intermediate prepared from high reactive polyisobutylene (Mn=1000) by thermal adduction process. The ashless dispersant produced from PIBSA possesses fine detergency and favourable low temperature sludge dispersion. Polyisobutylene Succinic Anhydride is a type of polyisobutylene succinic anhydride, also known as thermal adduction PIBSA. Polyisobutylene succinic anhydride is a lubricant additive that is commonly used in the automotive and industrial sectors. It is a derivative of 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 emulsifying agents for emulsion explosives. Used for preparation of processing aids for petroleum chemical plant Item Typical Value Test Method Appearance Transparent Viscous Liquid Visual Density(20℃),kg/m³ 900-1000 SH/T0604,ASTM D4052 Flash Point (COC),℃ ≥180 GB/T3536,ASTM D92 Kinematic Viscosity(100℃),mm²/s Report GB/T265,ASTM D445 Saponification Value,mg KOH/g >80 GB/T8021,ASTM D94 Free Anhydride,m% ≤0.7 MechanicalImpurities,m% ≤0.2 GB/T511 Company OverviewAt [Shanghai Minglan Chemical Co.,Ltd.], we specialize in high-performance lubricant additive packages, helping manufacturers develop next-generation engine oils, industrial lubricants, and specialty fluids. Our state-of-the-art R&D laboratory provides comprehensive formulation support, advanced testing, 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 lubricant industry. Whether you’re developing PCMO, HDDO, EV fluids, or industrial 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 lubricant additives. It’s not directly added to 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 (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 oil minimizes wear on engine components by preventing abrasive contaminants from contacting metal surfaces. Extended Oil Life: By maintaining 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. Water-in-oil emulsion explosive. US Patent 4,919,179. 1990.Ganguly S, Mohan VK, Bhasu VCJ, Mathews E, Adiseshaiah KS, Kumar AS. Surfactant–electrolyte interactions in concentrated water-in-oil emulsions: FT-IR spectroscopic and low-temperature differential scanning calorimetric studies. Coll Surf. 1992;65(4):243–256. doi:10.1016/0166-6622(92)80180-A. Article CAS Google Scholar Ghaicha L, Leblanc RM, Chattopadhyay AK. 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Article CAS Google Scholar Mata JP, Reynolds PA, Gilbert EP, White JW. Extended Q-range small angle neutron scattering from inverse micellar solutions of PIBSA—Micelle and molecular scattering. Colloids Surf A. 2013;418:157–164. doi:10.1016/j.colsurfa.2012.11.034. Article CAS Google Scholar David C. Thermal degradation of polymers. In: Bamford CH, Tipper CFH editors. Comprehensive chemical kinetics. Amsterdam: Elsevier; 1975. p. 1–173. doi:10.1016/S0069-8040(08)70333-9. Google Scholar Pirouz S, Wang Y, Chong JM, Duhamel J. Chemical modification of polyisobutylene succinimide dispersants and characterization of their associative properties. J Phys Chem B. 2015;119(37):12202–12211. doi:10.1021/acs.jpcb.5b04515. Article CAS Google Scholar Dimitrov P, Emert J, Hua J, Keki S, Faust R. Mechanism of isomerization in the cationic polymerization of isobutylene. Macromolecules. 2011;44(7):1831–1840. doi:10.1021/ma102645w. Article CAS Google Scholar Walch E, Gaymans RJ. Synthesis of low-molecular-weight telechelic polyisobutylene. Polymer. 1993;34(2):412–417. doi:10.1016/0032-3861(93)90098-U. Article CAS Google Scholar Warren RW, Gates DS, Driscoll GL. NMR identification of C11 to C40 branched hydrocarbons derived from the decomposition of polyisobutylene. J Polym Sci Part A-1 Polym Chem. 1971;9(3):717–746. doi:10.1002/pol.1971.150090312. Article CAS Google Scholar Lehrle RS, Duncan R, Liu Y, Parsons IW, Rollinson M, Lamb G, Barr D. Mass spectrometric methods for assessing the thermal stability of liquid polymers and oils: study of some liquid polyisobutylenes used in the production of crankcase oil additives. J Anal Appl Pyrol. 2002;64(2):207–227. doi:10.1016/S0165-2370(02)00032-3. Article CAS Google Scholar Walch E, Gaymans RJ. Telechelic polyisobutylene with unsaturated end groups and with anhydride end groups. Polymer. 1994;35(8):1774–1778. doi:10.1016/0032-3861(94)90855-9. Article CAS Google Scholar Chance RR, Baniukiewicz SP, Mintz D, Strate GV, Hadjichristidis N. Characterization of low-molecular-weight polymers: failure of universal calibration in size exclusion chromatography. Int J 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 manufacture of oil-soluble dispersants for lubricating oil applications and 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, dihydro-, 3-(polyisobutenyl)-2 Polyisobutenylsuccinic Anhydride 3-(2-Methylprop-2-En-1-Yl)Dihydrofuran-2,5-Dione Butyl rubber For more information on RB PIBSA, contact our team today! Physical PropertyUnitTest MethodTypical Value Specific Gravity (60°F) °F ASTM D 4052 0.92 Viscosity (100°C) cSt ASTM D 445 140 Density (60°F) lb/gal ASTM D 1250 7.72 Color, dilute - ASTM D 6045 3 Flash Point °F ASTM D 92 392 Total PIBSA Number mg KOH/g - 92 TDS Sheet SDS Sheet Introduction to Polyisobutylene Succinic 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 enhancing the viscosity index of lubricants, providing better performance across temperature ranges.Understanding the specifics of PIBSA is crucial for its effective application in industrial processes.PIBSA is available in various formulations, tailored to meet specific industry needs. These formulations differ based on:Molecular Weight: Affects 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 AnhydridePolyisobutene Succinic AnhydridePIB Succinic AnhydridePIBSA’s versatility makes it valuable in multiple sectors.In the lubricant industry, PIBSA is a key intermediate for producing:Dispersant Additives: Keeps particles suspended, preventing sludge and deposit formation.Detergent Additives: Cleans existing deposits within engines.Viscosity Index Improvers: Enhances lubricant performance across temperature variations.PIBSA-derived additives are used in fuels to:Improve Combustion Efficiency: 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 corrosive agents.Neutralizing Acids: Prevents acid buildup 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.comTel.: +86 18121501731Address: No.11 Sandun East Road, Zhouzhuang, Jiangyin, ChinaWebsite: www.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.AntioxidantsViscosity Index ImproversAnti-wear AgentsPIBSAUsed as emulsifiers and corrosion inhibitors in lubricants and metalworking fluids.Specialty chemicals for the paint and coatings industry, improving drying times and durability.Customized chemical formulations to meet specific industrial requirements.PIBSA TDS and MSDS: Available upon request to provide detailed product information.Product CatalogsApplication GuidesTechnical ArticlesIndustry Journals: Stay updated with the latest research and developments in lubricant technology.Jiangyin Longkang 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 weight characteristics and the chemical structure of chain-end groups. The bulk of the PIBs manufactured worldwide are highly reactive polyisobutylenes (HRPIBs) with –C(Me)=CH2 end-groups and low-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 and PIB analysis, examines actual catalytic approaches to PIBs, and describes recent studies on the functionalization and applications of HRPIBs and halogen-terminated PIBs. Keywords: cationic polymerization, exo-olefinic group, highly reactive polyisobutylene, 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 in 2021 [5] and is projected to reach USD 3.89 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)nCH2CH2NH2 (n = 1–4) and other amines [8,9,10]. The rate of the Alder-ene reaction depends significantly on the structure of the chain-end unsaturated fragment; the exo-olefinic group is the most reactive, and low-MW PIB containing >80% methylene fragments 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]. The synthesis of HRPIBs has been successfully commercialized; they are produced as ULTRAVIS (BP Chemicals, 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-Cl (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/dehydrochlorination, 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 necessitate the search for an alternative for toxic and corrosive BF3 [19] in the production of HRPIB. It is not 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 catalytic polymerization of IB with a formation of HRPIB had been discussed. From the 1990s to the early 2000s, studies of 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 may be divided into three generations. The first-generation 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 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 catalytic approaches to HRPIB in comparison with industrial 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 catalysts providing desired molecular weight characteristics and a sufficiently high content 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 study of PIBs have been developed long ago, but we thought it appropriate to include the results 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 seen in Figure 2, the exo-olefinic fragment >C = CH2 can be detected through the presence of singlets at δ = 4.68 and 4.89 ppm; the singlet at 5.19 ppm corresponds to the endo-olefinic group. The presence of –CMe2Cl end-groups can be detected through the signal of Me protons at δ = 1.68 ppm [29]. Effect of temperature on olefin end-group distribution during ionization of PIB-Cl with EtAlCl2 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 δ = 1.11 ppm (z) and 1.42 ppm (y) were assigned to the –CH3 and –CH2– protons of the main chain of PIB, respectively; the signal of –C(CH3)3 head group was observed at δ = 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, trisubstituted olefinic end-groups (C, D), tetrasubstituted olefinic end-group (E), and 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 [32]. Copyright (2011) American Chemical Society.The β-proton abstraction from the growing tertiary carbocation normally leads to exo- or endo-olefinic end-groups, –CH2C(CH3)=CH2 (A, δ = 4.64 and 4.85 ppm) or –CH2CH = C(CH3)2 (B, δ = 5.15 ppm). The two strong quartet resonances at δ = 5.17 and 5.37 ppm (c1, c2) and the intensive multiple resonances at δ = 2.85 ppm (e) were attributed to –C(CH3)=CH(CH3) (C for Z- and E- configuration) and –CH2C(CH3)=C(CH3)CH(CH3)2 (E) in PIB chains, respectively. The resonances at δ = 4.80 and 4.82 ppm were assigned to internal vinylene isomers F1 and F2, respectively. A weak singlet at δ = 5.12 ppm was attributed to the vinyl proton in –C(CH3)=CHC(CH3)2 (D). In addition, many minor undefined resonances were observed, such as single resonances at δ = 4.77 ppm, doublet resonances at δ = 5.01, 5.03 and δ = 5.06, 5.08 ppm, and triplet resonance at δ = 5.30 ppm. The formation of F1 and F2 is a

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 an indanyl ring when using 1,3-bis-(1-chloro-1-methyl-ethyl)-benzene as an initiator; and (b) mechanism of the synthesis of Cl–Allyl–PIB–Allyl–Cl in the tBu-m-DiCuOMe/TiCl4 initiating system via carbocationic polymerization in n-hexane/MeCl 60/40 (v/v) at 80 °C [68]. The very idea of developing new polymerization catalysts entails the use of Lewis base as a reaction component. The main potential advantage of these catalytic systems is the ability to conduct IB polymerization at temperatures above zero Celsius with a retention of high exo-olefin content in the reaction products. The first group of the catalysts, potentially able to replace BF3/ROH systems 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-olefin content) were observed when n-hexane was used as a reaction media [71]. In [33], Wu et al. have clearly demonstrated the marked difference in catalytic behavior of AlCl3/H2O and AlCl3/Bu2O catalytic systems. As can be seen in Figure 9, when using AlCl3/H2O vinylidene route to produce HRPIB is the minor one; tri- and tetra-substituted olefins are the main reaction 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 (A), trisubstituted olefinic end-groups (C), and tetrasubstituted olefinic end-group (E). 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.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 of 76.5–90% were obtained (the latter value depended on IB conversion; at high conversions the vinylidene 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 89–94% 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•Bu2O or AlCl3•iPr2O as co-initiators in n-hexane at elevated temperatures (−20 °C to 10 °C) and at high monomer concentrations (up to [IB] ~ 7.8 M) afforded low-MW PIBs (Mn ~1–8 kDa) with ĐM ~ 2, containing 70–85% exo-olefinic terminal groups [73]. The 1:1 complexes of AlCl3 with linear ethers were found to be stable at ambient temperatures; however, in the case of the AlCl3/iPr2O system, the formation of less 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 = 1:0.8) rapid polymerization of IB took place, and the distribution of end-groups was similar to one obtained with the ether-free initiating system. On the contrary, the use of slight excess of ether (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•R2O. Olefinic region (4.4–5.4 ppm) of 1H NMR spectra of PIBs obtained with the AlCl3•Bu2O/H2O initiating system in toluene at different AlCl3/Bu2O ratios: [co-initiator] = 22 mM; [IB] = 0.9 M. AlCl3/Bu2O ratio: (a) 1:0.8; (b) 1:1; (c) 1:1.2. Reprinted with permission from [73]. Copyright (2013) Elsevier B. V.During further studies of the complexes AlCl3•Bu2O and AlCl3•iPr2O, IB polymerizations were conducted at −20 to 20 °C in toluene or n-hexane media [74]. In both solvents, AlCl3•iPr2O showed higher activity and provided 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 increased. The use of a microflow reactor system for IB polymerization on AlCl3•iPr2O within ≤12 s was suggested by Lu et al. [75]. 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•Et2O, was studied recently in n-hexane by Lu et al. [79]. In this system, AlCl3•iPr2O was confirmed to be the key 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 Bu2O instead of iPr2O provided higher exo-olefinic content, but lowered the catalytic activity. However, 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 0.0075 0.0075 72 0.8 85 10 0.01 0.01 0.01 14 3.2 85 11 0.005 0.0025 0.0025 74 2.6 77 12 3 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 selectivity 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 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) on Mn of HRPIB were studied. Under optimized conditions (10 °C, N = 1600 min−1 and [M]0/[I]0 = 49) HRPIB with Mn = 2.55 kDa and an exo-olefin content of 85% was obtained. The discovery of AlCl3/R2O catalytic system encouraged the intensive investigations of Lewis acid/ether complexes in the synthesis of HRPIB. In 2011, Wu et al. studied the complexes of FeCl3 and a number of ethers (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 [R2O]/[FeCl3] ratio resulted in a decrease 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, [FeCl3•R2O] = 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 iPr2O 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 "*" represent excess iPr2O·TiCl4 complex; lines at 1.2 and 1.3 ppm are impurities in CS2. Reprinted 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 experiments. H2O/TiCl4/iAmOH initiating system exhibited high selectivity toward the cationic 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] re-initiated IB polymerization. Possible mechanism for synthesis of HRPIB via cationic polymerization of isobutylene with H2O/TiCl4/ROH (iPrOH or iAmOH) initiating system [89].In addition to etherates, the complex of FeCl3 with iPrOH was studied in IB polymerization [34]. 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 ≤ 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 and O(CH2CH2Cl)2 in tBuCl-initiated polymerization of IB, Faust and co-workers have found that only O(CH2CH2Cl)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 and O(CH2CH2Cl)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 tBuCl and catalyzed 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 ion equilibrium. The effect of impurities in the 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 temperatures showed that the reaction rate could be increased by increasing the polymerization 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 cations (resting states of the process, see Scheme 11). The example of tert-butyloxonium 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 the oxonium ion from EtAlCl2/O(CH2CH2Cl)2 + tBuCl and its thermal decomposition [96].From the point of view of industrial applications, the 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 (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 RAlCl2 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 ĐM was achieved by using a mixture of iPr2O and Et2O as an additive. The optimized conditions were [IB] = 5.8 M, [iBuAlCl2 preact.] = 38 mM, [Et2O] = [iPr2O] = 7.6 mM, [H2O] = 0.033 M, and 15 min at 10 °C. HRPIBs were obtained with more than 90% yield; they were characterized by an Mn of ~1 kDa, ĐM = 2.4–2.7 and an exo-olefin content of >80%. The use of AlCl3 or RAlCl2 in combination with ethers 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/iBuAlCl2·nR2O (n = 0–1; R2O = Bu2O, Hex2O, iPr2O) initiating systems in the synthesis of medium-MW HRPIBs. The H2O/iBu2AlCl system initiated slow IB polymerization with a formation of high-MW PIB (up to Mn = 55 kDa) with a ĐM of ~2.5 and an exo-olefin content of >85%. Addition of water increased the reaction rate, but almost did not affect the Mn and vinylidene selectivity. In the absence of 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 (Table 3, Entries 3, 8 and 13). The synergistic effect, observed in these 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 [iPr2O], M [Bu2O], M Conv., % 1 Mn, kDa 2 exo-, % 1 0.01 – 0.01 – 98 1.3 56 2 – 0.01 0.01 – 7 4.2 82 3 0.005 0.005 0.01 – 98 1.4 84 4 0.0025 0.0075 0.01 – 85 1.8 80 5 0.0075 0.0025 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 0.005 – 70 2.8 80 10 0.01 – – 0.01 28 2.8 77 11 – 0.01 – 0.01 99% of the bisphenol A (BPA) was extracted from the aqueous solution with a concentration of 200 mg•L−1. Other chlorinated, brominated, and alkylated 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-C6H3(CMe2Cl)3 initiator and FeCl4/iPrOH catalysts), followed by acylation with methacryloyl chloride, resulted in a highly reactive photo-crosslincable polymer that was used for matrix stabilization of quantum dots [164]. Synthesis of PIB telechelic prepolymers with various epoxide functionalities: (a) PIB aliphatic glycidyl ether; (b) PIB phenyl 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. Highly reactive 'Cl-allyl-PIB-allyl-Cl' 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 increasing the PIB diol concentration in the reaction mixture, a copolymer with an increased MW (>100 kDa), a tensile strength of ≈32 MPa, an elongation of ≈630%, 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 (δ-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 various compositions [175]. Commercial PIB-SA was introduced to polycondensation with glycerol oligomers 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 methacrlyc anhydride; the resulting amides were copolymerized 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 engine oil formulations. The development of new, cost-efficient and environmentally friendly catalysts 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 systems mainly based on the metal chloride/ether adducts—the first-, second-, and third-generation catalysts—according to the classification proposed by S. Kostjuk in 2021 [2]. Among the metal chloride/R2O catalytic systems, AlCl3/R2O could be a good alternative to BF3-based catalysts; however, the problem of low activity and poor solubility of the 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 hydrocarbon feeds instead of pure IB is a growing trend in modern technologies of HRPIB manufacturing [55,56]. 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 polymerization catalysts arise. Except for the problem of the resulting 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 HRPIB functionalization can be successfully applied in methylenealkane chemistry, and vice versa, especially in view of the progress achieved recently in catalytic transformations of methylenealkanes [182,183,184,185,186,187]. Conceptualization, I.E.N.; methodology, I.E.N.; software, I.E.N.; formal analysis, A.N.T.; investigation, I.E.N., S.A.K., M.S.C. and A.N.T.; resources, I.E.N.; data curation, I.E.N.; writing—original draft preparation, I.E.N., S.A.K., M.S.C. and A.N.T.; writing—review and editing, I.E.N.; visualization, I.E.N.; supervision, I.E.N.; project administration, I.E.N.; funding acquisition, I.E.N. All authors have read and agreed to the published version of the manuscript. Not applicable. Not applicable. The authors declare no conflict of interest. This research was carried out within the State Program of A.V. Topchiev Institute of Petrochemical Synthesis. 1.McDonald M.F., Jr., Shaffer T.D., Tsou A.H. Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Wiley; Hoboken, NJ, USA: 2016. Commercial Isobutylene Polymers; pp. 1–25. [DOI] [Google Scholar] 2.Vasilenko I.V., Kostjuk S.V. 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