





Review

A Bibliometric Survey on Polyisobutylene Manufacture

Jessica B. Alves ¹, Mateus K. Vasconcelos ², Lys H. R. Mangia ², Maxmiliano Tatagiba ², Juliana Fidalgo ², Daniela Campos ³, Pedro L. Invernici ², Marcio V. Rebouças ⁴, Marcio Henrique S. Andrade ⁴ and José Carlos Pinto ^{2,*}

¹ Programa de Engenharia de Nanotecnologia/COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-972, Brazil; jessica.alves@coppe.ufrj.br

² Programa de Engenharia Química/COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-972, Brazil; mvasconcelos@peq.coppe.ufrj.br (M.K.V.); lys@peq.coppe.ufrj.br (L.H.R.M.); maxmiliano@peq.coppe.ufrj.br (M.T.); jfidalgo@peq.coppe.ufrj.br (J.F.); pinvernici@yahoo.com.br (P.L.I.)

³ Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-972, Brazil; danielacampos.nave@gmail.com

⁴ Braskem S.A., Rua Lemos Monteiro, 120, 22° andar. Edifício Pinheiros One, Butantã, São Paulo 05501-050, Brazil; marcio.reboucas@braskem.com (M.V.R.); marcio.andrade@braskem.com (M.H.S.A.)

* Correspondence: pinto@peq.coppe.ufrj.br

Abstract: Polyisobutylenes (PIB) constitute a versatile family of polymer materials that have been used mainly as fuel and lubricant additives. Particularly, the current commercial demand for highly reactive polyisobutylene (HR-PIB) products motivates the development of new processes and procedures to produce PIBs with high polymer yields, narrow molar mass distributions and high vinyl contents. For this reason, a bibliometric survey is presented here to map and discuss important technical aspects and technological trends in the field of solution cationic polymerization of isobutylenes. It is shown that investigations in this field are concentrated mainly on developed countries and that industrial initiatives indicate high commercial interest and significant investments in the field. It is also shown that use of catalyst systems based on AlCl_3 and ether cocatalysts can be very beneficial for PIB and HR-PIB manufacture. Finally, it is shown that investigations search for cheaper and environmentally friendly catalysts and solvents that can be employed at moderate temperatures, particularly for the production of HR-PIB.

Keywords: polyisobutylene; PIB; HR-PIB; cationic polymerization



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1. Introduction

Polyisobutylenes (PIB) constitute a highly versatile family of saturated aliphatic polymer materials that are produced as commodity products, although in much lower volumes than other typical polymer commodities. PIBs were originally developed by BASF SE in 1931, presenting several important and characteristic properties, including low glass and crystallization temperatures (-60 and 5 °C, respectively), relatively high densities (0.9 g/mL), and low permeabilities for common small molecules [1–3]. PIBs are also characterized by good chemical resistance against strong oxidizers (such as ammonium hydroxide, peroxides and hydrochloric acid), corrosives (such as sulfuric acid and dilute hydrofluoric acid) and harsh chemicals (such as *n*-methylpyrrolidone), due to the inherent low reactive character of PIB materials [4]. Particularly, the weak dependence between the structural relaxation temperature and the viscosity, the wide mechanical segmental dispersion and the high degree of inelastic spreading are unique and very unusual when compared to other polymer materials, and can be associated with the high rates of structural relaxation [3]. Consequently, PIBs find numerous important commercial applications as food additives, chewing gums, additives for cosmetic products and raw materials for manufacture of lube additives, metalworking fluids, adhesives and a number of different materials used in

the construction sector (as sealants and electrical insulators, for example) [2,4]. Moreover, IB-based polymers with (multi-level) branched architectures, such as arborescent polymers and amphiphilic conetworks (APCN), present potential for use in wide ranges of applications, including microencapsulation, dispersion of chemicals and catalysts, manufacture of reactive polymers, modification of rheological properties of solutions and suspensions, and additivation of polymer processing operations due to the complex heterogeneous morphology, good swelling properties and extremely high mechanical strength [5–7].

The global polyisobutylene market was equivalent to USD 2.2 billion in 2020 [8] and is estimated to grow steadily at annual rates of 4.0%, motivated by the increasing demands from the automotive, pharmaceutical, fuel and chemical sectors. It is worth mentioning that new industrial applications demand PIB products with higher reactivity, even lower permeability to humidity and gases, high resistance to oxidation and enhanced chemical and thermal stability. Additionally, the sector also demands more sustainable processes and development of environmentally friendly PIBs [8]. As one might already expect, the properties of PIB products are highly dependent on molar mass averages and molar mass distributions. For this reason, the commercial applications of PIBs are usually divided into three large groups of materials, in accordance with the average molar masses: high (HM-PIB, $M_n > 120$ kDa), medium (MM-PIB, $40 \text{ kDa} < M_n < 100 \text{ kDa}$) and low (LM-PIB, $M_n < 5 \text{ kDa}$) molar mass PIBs [9]. Thus, the proper control of molar mass averages and distributions constitutes a critical point in PIB technologies. For this reason, as explained by Puskas et al., 2004, isobutylene polymers are produced commercially through solution cationic polymerizations, in order to assure the production of polymer grades with predictable and controllable molar mass distributions and stereochemical properties [10,11].

Although not important commercially today, PIBs have also been produced through radical polymerizations, as described in the literature. For example, Volkis et al., 2009 [12] and Volkis et al., 2012 [13] reported the use of this method using $\text{LiCB11}(\text{CH}_3)_{12}$ as catalyst and 1,2-dichloroethane or toluene as solvent for the synthesis of highly branched polyisobutylenes. Hero et al., 2021, [14] also reported the production of linear polyisobutylenes through free radical polymerizations in aqueous media, using cyclodextrin as a solubilizer.

Cationic isobutylene polymerizations are characterized by the very high reaction rates, which are associated with the chemical structure of the polymer chains and active reaction sites. The carbocationic nature of the chain termination is extremely reactive and sensitive to changes of the medium composition, which affects the propagation, chain transfer and termination steps. Therefore, quasilingiving carbocationic polymerizations are usually preferable in order to control the rates of reaction and the final polymer structure [11,15]. Faust et al., 1987 [15] introduced the quasilingiving polymerization assumption to describe the polymerization of olefins, considering the existence of reactive aprotic acidic sites and stable counterions (as esters) in the reaction medium, which can exert significant impact on rates of chain initiation, chain propagation and proton elimination.

The proposed reaction mechanism normally admits that the polymerization is initiated by a Lewis acid species. These species, normally called catalysts or co-initiators, are able to donate protons and interact with unsaturations present in monomer molecules, forming living ionic polymer chains that can initiate the polymerization of olefins. The commonest species used as catalysts are AlCl_3 , TiCl_4 and BF_3 [16]. The catalyst system usually involves a second chemical species, normally named co-catalyst or initiator, which is responsible for donating electrons to the catalyst, enabling the formation of the catalytic complex. Lewis bases are the commonest cationic polymerization co-catalysts, including water, alcohols and organic acids [16].

Besides the catalysts and co-catalysts, the solvent also plays a very important role in cationic olefin polymerization processes. As a matter of fact, the solvent is responsible for keeping the catalytic complex active and for controlling the activity of the reactive sites, which is closely related to the dielectric properties of the solvent and the relative solubilities of catalysts and co-catalysts in the reaction medium. It is also important to emphasize,

as discussed in the following sections, that cationic polymerizations are traditionally conducted in solution at extremely negative temperatures, in order to maintain the high catalytic activity [16].

The kinetic mechanism usually adopted to describe cationic polymerizations of olefins comprises four main steps (Table 1) [17]. Firstly, the catalytic complex is formed, and initiation of the polymer chain takes place (reactions I and II). The generated ionic species is then subjected to an equilibrium reaction step, where dormant and active species are present because of the limited solubility of the ionic species in the solvent (reaction III). This particular reaction step can be strongly influenced by the dielectric properties of the solvent. Eventually, when the vibrating ionic species are sufficiently apart, chain propagation takes place (reaction IV). It is important to balance the relative concentrations of living and dormant species to achieve a controlled quasiliving reaction mechanism. Chain transfer reactions (reactions V and VI) can also occur, when the ionic active center is transferred to a monomer or counterion molecule. Finally, termination (reaction VII) can occur spontaneously, being responsible for interruption of chain propagation and loss of catalyst activity [18].

Table 1. Reaction Mechanism Usually Adopted to Describe Isobutylene Polymerizations [19].

Reaction Steps	Kinetic Constants
Initiation	
(I) $I + X \leftrightarrow I^+$	k, k_t
(II) $I^+ + M \rightarrow P_1^+$	k_i
Propagation	
(III) $P_i \leftrightarrow P_i^+$	k_a, k_d
(IV) $P_i^+ + M \rightarrow P_{i+1}^+$	k_p
Chain Transfer	
(V) $P_i^+ + M \rightarrow \Lambda_i + P_{i+1}^+$	k_m
(VI) $P_i^+ + X^- \rightarrow \Lambda_i + P_{i+1}^+$	k_s
Termination	
(VII) $P_i \rightarrow \Lambda_i + I^-$	k_T

I is the Lewis acid, X is the Lewis base, I^+ is the catalytic complex, M is the monomer molecule, P_i is the dormant polymer species of size i , P_i^+ is the active polymer species of size i , Λ_i is the dead polymer chain and X^- is the counterion or a chain transfer agent [18].

After the polymerization step, many applications (such as lubricating oils additives, adhesives, putty glue and electrical insulating) demand the posterior functionalization of PIB chains, so that PIB chains must be reactive to some extent to make these applications feasible. This explains the current commercial demand for development of highly reactive polyisobutylene (HR-PIB) products and respective production processes [19]. Conventional PIB (C-PIB) and HR-PIB grades present distinct chemical structures, particularly regarding the position of the unsaturation bonds formed after the chain transfer and chain termination steps [11,15,19]. For C-PIB, most unsaturated double bonds are located internally in the chain (endo groups, sometimes more than 90% of the double bonds), whereas for HR-PIB, most unsaturated double bonds are located at the terminal chain end (exo groups, more than 70% of the double bonds) [20], which facilitates the subsequent functionalization reactions.

Figure 1 presents a simplified mechanism that explains the formation of C-PIB and HR-PIB chains through cationic polymerization of isobutylene. As already described, the first step comprises the initiation reactions, when the active carbocationic species are generated to allow the polymer chain growth. The addition of monomer molecules to the growing chain takes place at the ionic end group during the propagation step. Chain transfer can also take place, being characterized by hydrogen abstraction from the active chain end by monomer molecules. This ensures that the newly formed active sites will continue to propagate, keeping the characteristic high rates of the reaction system. Lastly, termination

or spontaneous chain transfer can take place through rearrangement of the carbon chain end or reaction of the reactive group with the counterion. Generally, PIB is produced through a living polymerization mechanism, so that the rate of chain termination is usually negligible and the growth of the cationic chain is limited by monomer consumption [19,21]. During termination and chain transfer steps, the nature of the produced unsaturated double bond is related to the charge distribution between the tertiary (leading to exo double bonds) and the secondary (leading to endo double bonds) carbon atoms [19,21,22]. In order to describe this very important kinetic effect, which explains the formation of C-PIB and HR-PIB chains, according to the current kinetic interpretations, the transfer of the cationic positive charge between neighboring carbon atoms must be described by an independent “charge walking step”, which is somewhat analogous to the well-known “chain walking” step of coordination polymerization mechanisms [23].

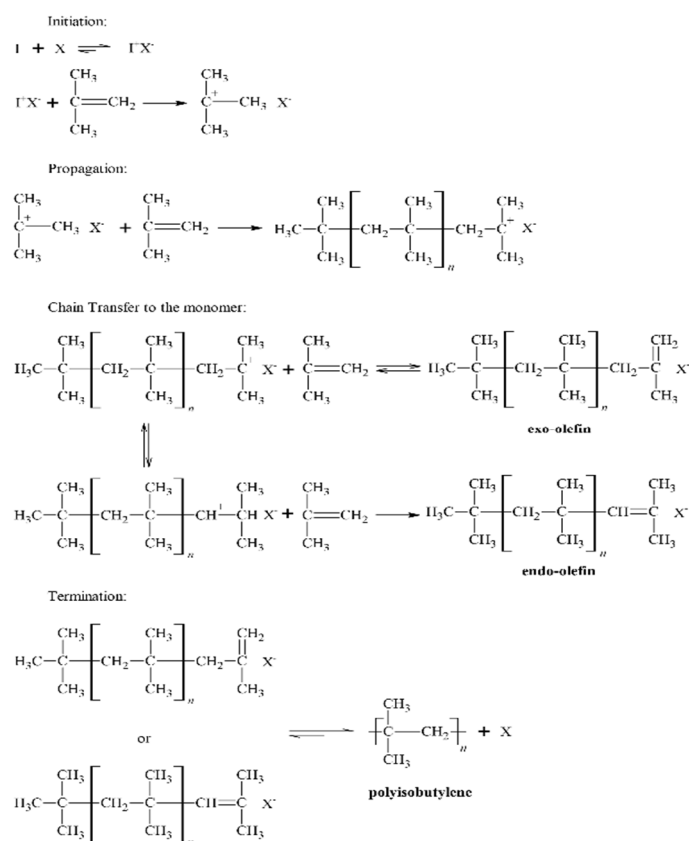


Figure 1. Mechanism for endo and exo-olefin end group formation in polyisobutylene chains [19,21]. “I” stands for the initiator and “X” for the counterion Lewis base.

Commercially, both HR-PIB and C-PIB are produced through similar cationic solution polymerization processes, although using different catalyst systems and reaction conditions [11,15,19,22]. As a matter of fact, the HR-PIB market is consolidated worldwide and involves applications in the packaging, automotive and industrial sectors, with an expected market value of USD 550 million per year by the end of 2030 [24].

Recently, Rajasekhar et al., 2020 presented a review on academic PIB research, with emphasis on HR-PIB, presenting recent advances on polymerization mechanisms and industrial practices, including the use of nonpolar solvents (usually cheaper and more easily handled), higher temperatures (which leads to less expensive and more convenient industrial processes) and industrial raffinate (C4 raffinate) as feed stream (usually available at oil-based chemical plants and avoiding purification of feed streams). Moreover, multiple strategies were suggested for development of new catalyst systems that can eventually replace the traditional and toxic catalyst BF_3 [22]. In fact, other studies have already

reported that alternative Lewis acid catalytic complexes (based on the AlCl_3 catalyst and distinct ether co-catalysts) are already being applied industrially [19].

Based on the previous paragraphs, Table 2 summarizes the main properties, industrial players, and applications of commercially available PIB materials. As one can see, PIB products are employed in multiple economic sectors, reflecting their commercial and economic importance.

Table 2. Main characteristics, properties, and players of commercially available PIB products.

PIB Grade	Characteristics and Properties	Main Applications	Main Industrial Players	Production Region
C-LMPIB	$M_n < 5$ kDa endo groups < 90%.	Lubricant additives, two-stroke engine oils, insulating oils, adhesives, sealants [25], surfactants and dispersants [26].	Braskem, BASF SE, Exxonmobil, ENEOS, CNPC, Lanxess, Lubrizol, Daelim, Petronas [27].	
C-MMPIB	$40 < M_n < 100$ kDa Exceptionally low permeability, good thermal and oxidative stability, chemical and ozone resistance, high mechanical dampening and tack [10].	Viscosity modifiers, fuel and lubricating oil additives, tack improvers in adhesive formulations and primary binders in caulking and sealing compounds [10].	Braskem, BASF SE, Zhejiang Shunda New Material Co., JX Nippon Oil and Energy Shandong Hongrui Petrochemical Co. [27].	North America, Europe, Asia-Pacific, South America, Middle East and Africa [28].
C-HMPIB	>20 kDa Elastomers with low density, low permeability and excellent electrical properties [25].	Adhesives and sealants, lubricant and grease manufacturers, metalworking, cosmetics and mining [29].	Braskem, BASF SE, Lanxess AG, Daelim [27].	
HR-LMPIB	<5 kDa $75 < \text{exo groups} < 85\%$ [30].	Intermediates for preparation of lubricant additives and fuels [31].	Braskem, BASF PETRONAS Chemicals, Saudi Aramco—Daelim [31].	
HR-MMPIB	$55 < M_n < 80$ kDa exo group > 85% PID < 2.5 [32,33].	Hydraulic fluid, greases and emulsifiers [31].		Asia Pacific, South East Asia [31].
HR-HMPIB	$M_n > 120$ kDa exo group > 85% [31].	Adhesives, sealants and wrapping films [31].		

Despite the commercial relevance, well-established industrial production processes and worldwide applicability of PIB products, a comprehensive bibliometric survey of the literature available in this field is not available. For this reason, the following sections of the present work map, measure, describe and discuss important technical aspects and technological trends in the field of solution cationic polymerization of isobutylenes, aiming at the production of both C-PIB and HR-PIB products. Among the technical aspects, the most important process operational parameters, including the selected Lewis acids, Lewis bases, solvents and temperatures are highlighted, as these parameters exert significant influence on the course of the polymerization and, consequently, on the final polymer properties.

2. Methods Used for the Literature Survey

2.1. Papers

The conducted bibliometric study was based on electronic search tools. Web of Science and Scopus were used to explore academic papers. The ISI Web of Science indexes 9370 science journals with worldwide journal coverage [34], while Scopus counts with 23,452 peer-reviewed journals and more than 5000 international publishers [35]. Thus, both selected electronic databases can provide extensive and reliable references to conduct a comprehensive analysis of academic papers in our field of study.

The Scopus database was used to collect academic papers written in English in the field of isobutylene polymerization. The initial search was carried out on 7 January 2020, and has been complemented since then, based on the references of downloaded papers and information provided by published journals. At first, the used search terms were “isobutylene polymerization” OR “isobutene polymerization”. In order to refine the results, the following subject areas were excluded from the initial search: “PHYS”, “BIOC”, “PHAR”, “ENER”, “ENVI”, “COMP” and “ENGI”. Only articles already published in scientific journals were considered to perform the bibliometric analysis, which considered papers published from 1960 to 2020.

Although comprehensive reviews of papers published in languages other than English has not been performed, it is important to emphasize that relatively few papers regarding PIB manufacture were published in other languages, most of them more than 30 years ago, and that the respective scopes were very similar to the ones presented in the papers written in English. Consequently, it can be assumed that the English language does not constitute a relevant drawback for the present study.

The Web of Science database was also used to analyze academic publications written in English in the field of isobutylene polymerization. The initial search was carried out on 4 April 2020, and has been complemented since then, based on the references of downloaded papers and information provided by published journals. In this case, the used search terms were “isobutylene AND (polymerization or polymerisation)” OR “isobutene AND (polymerization or polymerisation)” in the topic field. Only articles already published in scientific journals were considered to perform the bibliometric analysis, which considered papers published from 1960 to 2020. The following subject areas were excluded from the initial search: “Electrochemistry OR Medical Laboratory Technology OR Microbiology OR Physics OR Nuclear Science Technology OR Oncology OR Optics OR Biodiversity Conservation OR Crystallography OR Radiology Nuclear Medicine Medical Imaging OR Food Science Technology OR Biophysics OR Immunology OR Computer Science OR Infectious Diseases OR Mathematical Computational Biology OR Biochemistry Molecular Biology OR Cardiovascular System Cardiology OR Hematology OR Ophthalmology OR Energy Fuels OR Pathology OR Instruments Instrumentation OR Agriculture OR Plant Sciences OR Biotechnology Applied Microbiology OR Public Environmental Occupational Health OR Cell Biology OR Surgery OR Pharmacology Pharmacy”.

For the purposes of the present study, papers obtained from both databases were combined and downloaded. As informed previously, this combined list of publications has been complemented since then, based on the references of downloaded papers and information provided by published journals. Initially, the manuscripts were grouped in terms of the categories described in Table 3 to conduct the bibliometric analyses.

Table 3. Categories used for bibliometric analyses of published papers in the present study.

#	Category	#	Category
1	Year of publication	6	Lewis acid
2	Journal	7	Lewis base
3	Institution/applicant	8	Solvent
4	Country	9	Temperature
5	Number of citations	10	Vinyl content

Categories #3 and #4, Institution and Country, respectively, were reported in accordance with the affiliation of the last author. The Number of Citations, category #5, was obtained from the database at the moment of paper downloading and data acquisition and, therefore, are not necessarily synchronized. Later, the Number of Citations was used to determine the five most influential works in the field, assuming that this index can be used to measure the impact of the article on the technical and scientific communities. Cate-

gories #6 to #9 are related to process operation conditions, which are needed to evaluate the conditions used most often to perform isobutylene polymerizations in the academic environment. In particular, category #10 was added in order to identify papers involved with the production of HR-PIB (more than 70% of exo groups). It is worth mentioning that papers focused on the copolymerizations of isobutylene with other monomers and the synthesis of new catalyst systems were only considered in the bibliometric analysis when the authors provided information about the operation and characterization procedures used to produce and characterize the properties of the obtained isobutylene homopolymer.

2.2. Patents

The conducted bibliometric study was also based on electronic search tools, and ESPACENET was used to explore published patents. This patent database indexes patents from most countries with worldwide coverage of innovation and development. Thus, these references are presented as reliable to conduct a comprehensive analysis of academic articles in our field of study.

Patents written in English, German and French were collected in the area of isobutylene polymerization. The initial search was carried out on 7 January 2020, and has been complemented since then, based on information provided by published journals and patents, country or region holding the technology and patent applicants and players. Initially, the search terms used were “isobutylene AND polymerization” OR “isobutene AND polymerization”. Only patents already published, regardless of their status, were considered for the bibliometric analyses, which considered papers published between 1960 and 2020. For the purposes of the present study, the obtained patents were grouped according to the categories described in Table 4 to carry out the bibliometric analyses.

Table 4. Categories used for bibliometric analyses of published patents in the present study.

#	Category	#	Category
1	Year of publication	6	Lewis base
2	Applicants/Players	7	Solvent
3	Status	8	Temperature
4	Country	9	Vinyl content
5	Lewis acid		

Category #3 was classified in terms of three possible outcomes: active, pending and not active. Active status includes the following terms exposed as status in the “active”, “application granted” and “ip right grant” patents. Pending status includes the following terms displayed as status in the “pending”, “application filling” and “searching and examination” patents. Not Active status includes the following terms exposed as status in the patents: “withdraw”, “expired”, “ip right cessation”, “revoked”, “application discontinuation”. Category #4 was reported considering the country of origin where the considered process was developed. Categories #5 to #8 are related to process operation conditions, which are needed to evaluate the conditions used to perform isobutylene polymerizations in the academic and industrial environments. In particular, Category #9 was added in order to identify patents involved with the production of HR-PIB (more than 70% of exo groups). These process operation conditions were based on the claims that form the patent description.

2.3. Statistical Analyses

Standard statistical and correlation analyses were performed with help of the Statistica 7.0 software (TIBCO Software Inc., Palo Alto, CA, USA). Unless stated otherwise, all statistical evaluations were performed within the confidence level of 95%.

3. Results and Discussions

3.1. Papers

After the data mining phase, the final set of downloaded documents comprised 341 published papers, including 86% of the papers related to C-PIB technologies and 14% of the papers related to HR-PIB technologies. This scenario illustrates the more traditional use of C-PIB products and the largest commercial market of C-PIB materials, despite the growing market share of HR-PIB grades.

3.1.1. Yearly Distribution

Figure 2 shows the evolution of the annual number of published articles involving PIB materials in the past decades. As a whole, the number of published papers per year is not very impressive, which reflects the relatively small number of researchers involved with investigations in this field, when compared with other areas of knowledge. Particularly, in the 1990s there was an apparent increase in academic interest in this field, which can be related to the appeal of the newly developed HR-PIB products and to implementation of worldwide policies, encouraging the development of environmentally safe practices and imposing restrictions on vehicular polluting emissions [8]. As a matter of fact, functionalized HR-PIB materials can be used as fuel and lubricant additives for enhancement of engine performance, diminishing the production of particle residues and reducing the emissions of hydrocarbons and particles [22]. For this reason, laws are enforcing the use of these HR-PIB based materials in many countries and providing an additional push for development of HR-PIB technologies. Nevertheless, the reduction in the number of scientific publications in the field over the last decade indicates that the available technologies are mature and that new breakthroughs are needed to encourage investigations and scientific development in this area.

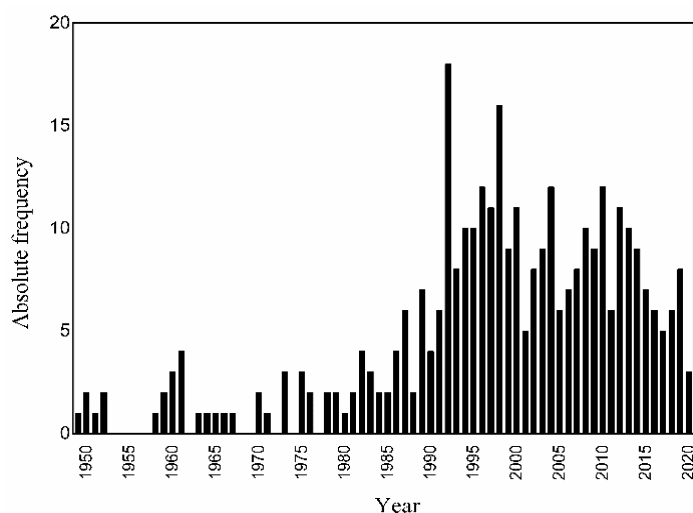


Figure 2. Number of published scientific papers in the field of PIB manufacture over the years.

3.1.2. Distribution of Scientific Journals

Table 5 presents the 10 journals used most frequently by researchers to publish the results of PIB investigations. As shown in Table 5, papers related to PIB are concentrated in scientific journals connected to materials science, chemistry and engineering, although journals connected to physics and catalysis have also been used less frequently for communication of catalyst developments and advances in the interpretation of reaction mechanisms. Nevertheless, significant concentration of papers was observed in the journals “*Macromolecules*” and “*Journal of Polymer Science (Part A: Polymer Chemistry)*”, with 76 and 49 papers, respectively. When the quantitative (CiteScore and JIF—Journal Impact Factor) [36] and qualitative (SNIP—Source Normalized Impact per Paper) [36] metric

indicators are used to evaluate the impact of the research done in the field of interest, one can conclude that the selected journals can be regarded as influential (high citation scores) but that investigations published in the field of interest are much less influential than the average papers published in those journals (much lower SNIP scores). This reflects the much smaller size of the PIB investigation communities, when compared to other areas of research, as stated previously.

Table 5. Journals used most frequently to publish investigation results in the field of isobutylene polymerization between 1960 and 2020.

Ranking	Journal	Absolute Frequency	JIF ¹ (2019)	Cite Score (2019)	SNIP ² (2019)
1	<i>Macromolecules</i>	76	5.918	10.2	1.464
2	<i>Journal of Polymer Science, Part A: Polymer Chemistry</i> <i>Incorporating: Journal of Polymer Science, Part C: Polymer Letters</i> <i>Formerly known as Journal of Polymer Science, Part A-1, Polymer Chemistry</i>	49	2.930	5.2	0.740
3	<i>Polymer Bulletin</i>	33	2.014	2.7	0.735
4	<i>Journal of Macromolecular Science—Pure and Applied Chemistry</i>	18	1.349	2.3	0.640
5	<i>Russian Chemical Bulletin</i> <i>Formerly known as Bulletin of the Academy of Sciences of the USSR Division of Chemical Science</i>	15	1.062	1.8	0.619
6	<i>Polymer</i> <i>Incorporating: Polymer Communications; Computational and Theoretical Polymer Science</i>	15	4.231	6.9	1.255
7	<i>European Polymer Journal</i>	11	3.862	6.1	1.188
8	<i>Polymer Chemistry</i>	10	5.342	9.0	1.057
9	<i>Physical Chemistry Chemical Physics</i> <i>Formerly known as Transactions of the Faraday Society</i>	9	3.430	6.3	0.980
10	<i>Macromolecular Chemistry and Physics</i> <i>Incorporating: Acta Polymerica</i>	8	2.335	4.3	0.625

¹ JIF: Journal Impact Factor. ² SNIP: Source Normalized Impact per Paper.

3.1.3. Distribution of Countries

Figure 3 displays the countries of research institutions that published scientific papers regarding the PIB manufacture. As one can see, American institutions published approximately 42% of the articles in the field, followed by Germany and China, with approximately 10% each. Not surprisingly, this is related to the most important commercial players in the field (as shown in Table 2) and to the commercial demand for this material in these countries.

3.1.4. Distribution of Research Institutions

Table 6 shows the research institutions that published scientific papers regarding PIB manufacture most frequently. As expected, the research institutions with most of the publications in the area of PIB are American universities (The University of Akron, University of Massachusetts Lowell and The University of Southern Mississippi). Although they do not appear among the main countries in publications, a Czech institution (Czech Academy of Sciences) and a Belarusian institution (Belarusian State University) appear among the most productive institutions in the analyzed field. In addition to these ones, other relevant Chinese, Canadian, German and Russian institutions could be detected in the area.

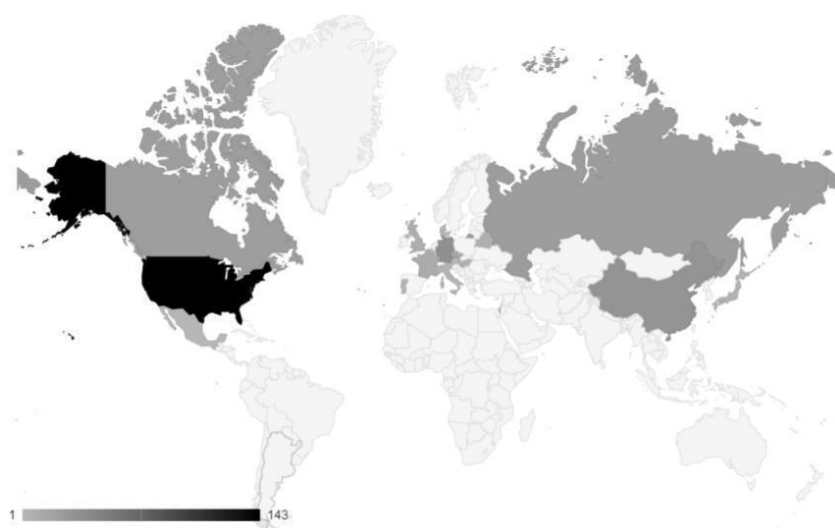


Figure 3. Distribution of scientific papers regarding PIB production between 1960 and 2020.

Table 6. Research institutions that published investigation results in the field of isobutylene polymerization most frequently between 1960 and 2020.

Ranking	Institutions	Country	Absolute Frequency
1	The University of Akron	USA	44
2	University of Massachusetts Lowell	USA	36
3	The University of Southern Mississippi	USA	31
4	Beijing University of Chemical Technology	China	18
5	Czech Academy of Sciences	Czech Republic	17
6	Belarusian State University	Belarus	12
7	Moscow State University	Russia	12
8	Queen's University	Canada	12
9	Technical University of Munich	Germany	9
10	Western University	Canada	9

3.1.5. Operation Parameters for Isobutylene Polymerizations

PIB manufacture technologies may depend on numerous distinct operation variables, although the most important ones are the Lewis acid catalyst, the Lewis base co-catalyst, the solvent and the temperature, as described in the following subsections.

Lewis Acid Catalysts

Figure 4 shows the citation frequencies of catalysts employed most often for manufacture of both C-PIB and HR-PIB grades. As one can see, most analyzed catalysts have been used for manufacture of both C-PIB and HR-PIB products, although with different frequencies. The catalysts reported most usually for isobutylene polymerizations are TiCl_4 , BCl_3 , AlCl_3 and SnCl_4 because of their well-known high catalytic activities [25,37]. Among these catalysts, TiCl_4 was cited in almost 35% of the analyzed papers for manufacture of C-PIB. Surprisingly, although BF_3 has been widely used for production of HR-PIB in industrial plants, this catalyst has not been used very frequently in scientific publications, possibly because of safety issues and difficult handling [19,22].

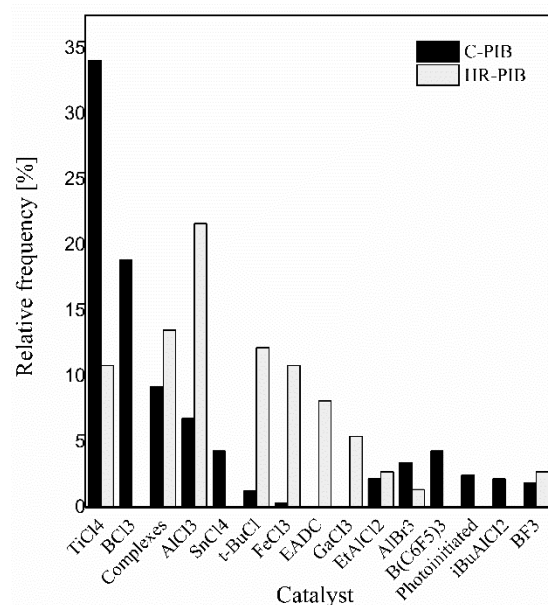


Figure 4. Frequencies of catalyst citations in scientific papers related to C-PIB and HR-PIB manufacture. (EADC: Ethylaluminum dichloride).

Although TiCl₄ has been the most cited Lewis acid catalyst since the 1950s, the steady decrease in the number of citations has also been observed in the last 10 years, indicating maturation of this technology and replacement by other catalysts. TiCl₄-based catalyst systems are efficient to produce C-HMPIBs, although requiring cryogenic temperatures to control the catalyst ionization more effectively [38–42]. Additionally, its toxic and corrosive nature constitutes a drawback for industrial applications, demanding expensive procedures to improve safety handling requirements and waste disposal [42]. For this reason, the declining interest in this catalyst can possibly be associated with the search for more environmentally safe practices. Besides, the use of TiCl₄ as co-initiator makes the control of the average molar masses difficult, as the isomerization of polyisobutylene chains can be significant during prolonged polymerization times [31,43,44]. Consequently, the production of TiCl₄-based HR-PIBs with vinyl contents above 80% has been seldomly reported in the literature [45]. In fact, only 10% of the papers regarding HR-PIBs reported the use of TiCl₄ for synthesis of the polymer.

As in the case of TiCl₄, BCl₃-based catalyst systems also exerted influence on academic research related to C-PIB production, especially in the 1990s [15,32,33,46]. The interest was focused mainly on the living polymerization of isobutylene and production of low molar mass telechelic PIB products [26,28,33,47]. This can be associated with the low stability of the intermediate BCl₄ that leads to rapid termination of active PIB chains, forming a chlorinated end group [27,29,30,32].

Catalyst systems involving organic boron complexes were cited in almost 9% of the papers that investigated the production of C-PIB grades. Weak Lewis acids, such as B(C₆F₅)₃ [48–54] and [Ph₃C][B(C₆F₅)₄] [55,56], have been described as efficient catalysts for C-PIB production because of their excellent single-site catalyst performances and ability to produce materials with high average molar masses (M_n of 10⁵ g.mol^{−1}) under mild reaction conditions and short reaction times (less than 60 min).

Currently, there is significant demand for replacement of the BF₃ catalyst for commercial production of HR-PIB [57] due to safety issues (BF₃ is very toxic) and difficulties to handle this halogenated gas, which leads to high operation and maintenance costs and expensive and dangerous treatment of effluents [58]. As an alternative, many investigations have been reporting the use of the AlCl₃ catalyst for production of HR-PIB (almost 21% of the articles related to manufacture of HR-PIB), especially because this catalyst has also been

used for long time to prepare C-PIB commercially [59], although only 10% of the papers related to production of C-PIB cited the use of the AlCl_3 catalyst.

The use of the AlCl_3 catalyst has been reported for manufacture of HR-PIB since 2010, which indicates that this indeed constitutes a new trend in the PIB technology [25,59]. Particularly, different researchers have reported contents of exo groups between 80 and 95%, for polymer materials produced in presence of oxygenated co-catalysts (as described in the next section) at mild conditions, short reaction times and with narrow molar mass distributions [25,59]. Consequently, AlCl_3 constitutes a promising alternative to replace the BF_3 catalyst in the near future. It is important to recall that the isobutylene polymerization catalyzed by AlCl_3 is usually very fast, and consequently highly exothermic and difficult to control, requiring the association with weak bases for selective electron abstraction and production of HR-PIB [60–63]. On the other hand, it offers convenient operation at relatively mild temperatures [43,60].

The use of solvent-ligated complex catalysts also constitutes a promising strategy to prepare HR-PIB through cationic polymerizations performed under mild conditions, in particular when the metal complexes (normally based on Mn, Ni, Cr, Co, Cu, Zn, Mo, Ga and Fe) are associated with weakly coordinating counteranions (WACs) [64–72]. The use of these compounds was cited in 13% of the papers related to the production of HR-PIB grades, where the high reactivity of the metal complexes was always highlighted.

Figure 4 also shows that about 10% of the analyzed papers related to HR-PIB manufacture cited the use of tert-butyl chloride (t-BuCl) or iron chloride (FeCl_3) as catalysts. In these cases, various authors reported the simultaneous combination of high vinyl contents (higher than 70%) and high monomer yields (monomer conversions between 80 and 100%) for short reaction times, when n-hexane was used as solvent with these catalysts [73–76].

The uses of ethylaluminum dichloride (EADC), GaCl_3 and other Lewis acid catalyst systems have also been reported by considerable fractions of the analyzed papers, as shown in Figure 4 [74,77]. The many Lewis acid compounds that have been tested to produce PIB materials, especially in the last two decades, illustrate the efforts that are still being made to select more efficient and viable alternatives to replace the more conventional catalysts in these processes [68,71,72,78–80]. Generically, the development of new catalysts pursues the combination of high activity and selectivity, cost reduction, easy handling and possible operation at mild conditions [59,65,76,81].

Lewis Base Co-Catalysts

In order to facilitate the quantitative analyses, the Lewis base co-catalysts described in the analyzed papers were classified in terms of their active functional groups. Figure 5 presents the relative frequencies of the main chemical functions used in the Lewis base co-catalysts. Organic halides (21%) and pyridine (22%) represent the most frequent Lewis base co-catalysts reported in papers related to production of C-PIB, while ethers (38%), alcohols (16%), pyridine (10%), and other inorganic compounds (10%) represent the most frequent Lewis base co-catalysts reported in papers related to production of HR-PIB. Thus, ether compounds have been the commonest Lewis base co-catalysts used in HR-PIB studies. On the other hand, hydrocarbons, esters, organometallic compounds and phenol have been used as co-catalysts for both technologies, while phthalates have been used exclusively for C-PIB reactions and benzene and nitriles have been used as co-catalysts only for manufacture of HR-PIB products.

For TiCl_4 -based systems, 2,6-di-tert-butylpyridine (DtBP) is the most cited co-catalyst, regarded as a strong Lewis base in the gas phase. DtBP acts as a proton trap in isobutylene polymerizations to avoid chain transfer and reversible termination steps, being commonly used to confer controlled/living characteristics to TiCl_4 -based C-PIB technologies [82,83]. However, Bae et al., 1998, [84] and Simison et al., 2006, [85] also reported the successful use of DtBP as Lewis base for HR-PIB production. The use of strong bases with the AlCl_3 catalyst was also evaluated for production of HR-PIB grades, but the researchers observed the decrease in monomer conversion and the exo vinyl content with these catalyst

systems [43,86]. This certainly illustrates the importance of evaluating synergetic effects among the different constituents of the initiation system.

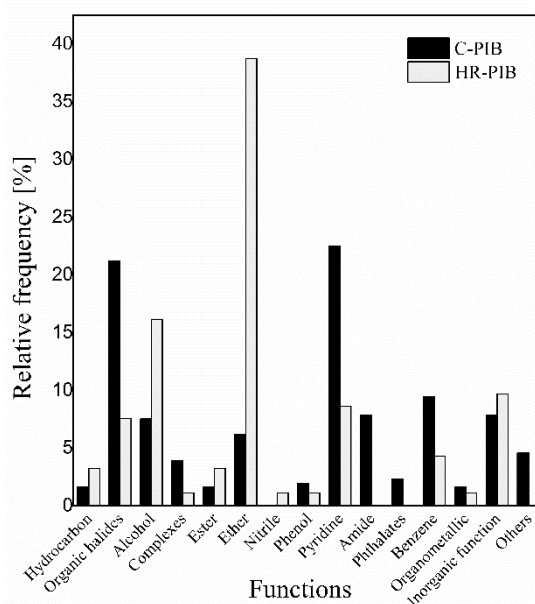


Figure 5. Frequencies of co-catalyst citations in scientific papers related to C-PIB and HR-PIB manufacture.

Organic halides accounted for 21% of the cited co-catalysts in papers related to C-PIB, although the best performances can be assigned to 2-chloro-2,4,4-trimethylpentane (TMPCl), which has been used mainly to perform isobutylene polymerizations in association with the TiCl_4 catalyst at cryogenic conditions [87–91]. TMPCl has also been used to study fundamental kinetic aspects of polymerization mechanisms because it allows the adequate control of the polymerization rates and the production of more uniform polymers [90,91]. Similarly, studies reporting the use of DtBP as co-catalyst and slow rates of polymerization to investigate aspects of the reaction kinetics can also be found in the field of carbocationic polymerization [38,84,87,92,93]. For all these reasons, the use of both DtBP and TMPCl as co-catalysts can be regarded as consolidated in the field of isobutylene cationic polymerizations.

Ether compounds (38%) have been largely used as Lewis base co-catalysts for synthesis of HR-PIB, although diisopropyl ether (Pr_2O) [58–60,94,95], bis(2-chloroethyl) ether (CEE) [96] and dibutyl ether (Bu_2O) [59,60] are the ones cited most often, usually in association with the AlCl_3 co-catalyst. This is probably due to the fact that ethers are known to form well-defined complexes with AlCl_3 [97]. The use of ether compounds leads to increase in the exo vinyl contents of the PIB products, as complexes formed with AlCl_3 are efficient to stabilize the carbenium ions, leading to high exo vinyl contents (>90%) at mild temperatures [98]. It is important to emphasize that the chain transfer step is extremely relevant in HR-PIB polymerizations, as the exo double-bond and a new protonated monomer result from the chain transfer reaction promoted by the ether [85]. Investigations carried with ethers of different basicities and with distinct ether/catalyst ratios indicated the enormous influence of basicity (and β -protons abstraction) on the average molar masses, exo vinyl contents, reaction rates and monomer conversions due to the modification of the reactivity and selectivity of the growing cations [37,60,86].

2-phenyl-2-propanol (CumOH) [43,47,99], tert-butanol (tBuOH) [73,100], tert-amyl alcohol (AmOH) [100,101], and isopropyl alcohol (PrOH) [45,75,102] were some of the alcoholic compounds also used as co-catalysts to perform isobutylene polymerizations. These compounds were cited as co-catalysts by many authors to produce HR-PIB products with exo vinyl contents higher than 80% [43,73,86,102].

Water is a peculiar additive that has been used as co-catalyst in isobutylene polymerizations because of its many known advantages, such as low cost and non-toxicity [81,86,95,103–105]. In the field of HR-PIB, the use of water has been extensively investigated [43,45,71,106]. Particularly, many authors observed that low concentrations of water did not affect the monomer conversions significantly [43,75,95,104,107], although at least one paper reported that addition of water might indeed affect the rates of polymerization [96]. Additionally, some authors reported that polymer materials with high exo vinyl contents (>80%) and narrow molar mass distributions can be produced at mild reaction temperatures (from -40 to 30 °C) using water as one of the key components of the catalyst system [43,104,107]. As a matter of fact, water can exert different and contradictory effects on the analyzed carbocationic reactions, depending on the analyzed catalyst system, due to participation in isomerization and chain termination reaction steps [43,62,74,77,95].

It is important to emphasize that many of the analyzed articles investigated the concomitant use of more than one co-catalyst in the initiation complex, although the observed results and trends have been essentially the ones already reported. Most of these investigations have been carried out as attempts to improve the selectivity of β -protons abstraction for catalytic chain transfer steps, and therefore to improve the control over the exo vinyl content of the obtained products [22,61,93,96].

Solvents

The 10 most frequently used solvents for each technology (C-PIB and HR-PIB), as reported in scientific publications, are presented in Figure 6. It must be highlighted that some solvents have been used in both technologies, which is not so common regarding Lewis acid catalysts and Lewis base co-catalysts. Particularly, both polar (55% of the citations) and nonpolar (45% of the citations) solvents have been used almost equally for production of C-PIB, although nonpolar solvents (64% of the citations) have been used more frequently for HR-PIB syntheses than polar solvents (36% of the citations). Among the reported nonpolar solvents, hexane and toluene are the ones cited most often, while dichloromethane (DCM) and chloromethane (CM) were the commonest ones among the polar solvents. The selection of the most appropriate solvent is strongly associated with the solubility of the Lewis acid catalyst and Lewis base co-catalyst in the reaction medium, as the solvent plays significant roles on solvation and stabilization of the carbocations [97]. Additionally, environmental effects, adequacy of safety procedures and practices affect the selection of the best suited solvent to conduct the isobutylene polymerization reaction [11].

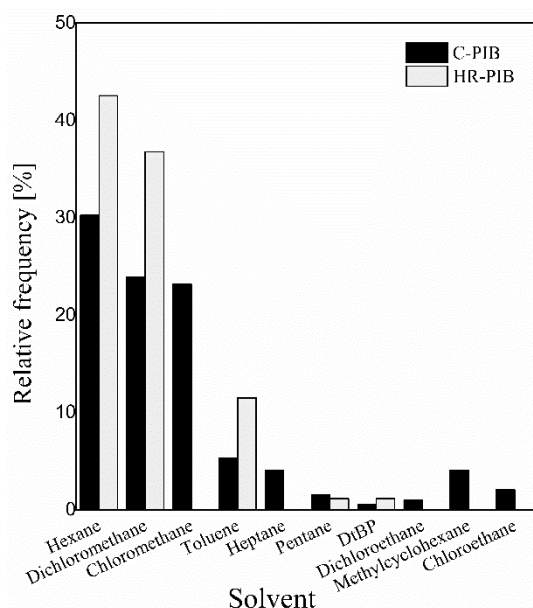


Figure 6. Frequencies of solvent citations in scientific papers related to C-PIB and HR-PIB manufacture.

The use of polar solvents favors the dissociation of the ionic polymer chains and increases the solubility of Lewis complexes and active species in the reaction medium, facilitating chain propagation reactions and increasing the reaction rates [15,64,108,109]. Consequently, polar solvents often boost the catalyst activities, also leading to faster rates of ionization and slower rates of chain termination, resulting not only to higher rates of polymerization but also to products with higher average molar masses [15,40,110]. This behavior has been characterized in detail in C-PIB polymerizations [15].

Nonpolar solvents, such as hexane and toluene, promote slower reaction rates as active species tend to present poor solubility in these solvents, consequently reducing the catalyst activities [13,65,111]. This fact favors the enhanced control of the reaction, as the lower rates of polymerization also lead to lower rates of heat release and better temperature control [13,65,111]. Besides, the use of nonpolar solvents can also be advantageous for industrial operation because it prevents the undesired production of toxic chlorinated residues.

It is important to note that most reported strategies that seek to balance the appropriate rates of polymerization and the desired set of polymer properties make use of (i) a single nonpolar solvent with highly efficient initiator complexes or (ii) mixtures of polar and nonpolar solvents [108,112–114], especially regarding the production of HR-PIB [39,43,74,108,115].

The use of TiCl_4 , the most reported Lewis acid catalyst, has been regularly reported in association with polar solvents, which can increase the concentration of active centers, resulting in a dormant and an active species connected by a mobile equilibrium [15]. As AlCl_3 complexes usually present poor solubility in nonpolar solvents due to the strong acidity, the use of these catalysts usually demands the use of solvent mixtures, higher initiator concentrations and high monomer concentrations [62,86,116]. However, GaCl_3 or FeCl_3 complexes can be used to produce HR-PIB grades in nonpolar solvents [80,81,103,117].

Temperatures

A wide range of reaction temperatures has been identified during the bibliometric analyses of the scientific articles. In order to facilitate the interpretation of the data, the temperature range was divided into intervals of 10 °C. Figure 7 shows the temperatures reported for C-PIB and HR-PIB syntheses with the respective frequencies. C-PIB reactions have been performed mostly at exceptionally low temperatures (from −80 to −30 °C), whereas HR-PIB reactions have been investigated at relatively higher temperatures (from −20 to 30 °C). As HR-PIB products have been investigated more lately, this also reflects the continuous trend pursued by commercial operations to shift the reaction temperatures towards more convenient and milder reaction conditions, as a strategy to reduce the operation costs.

As one might already expect, the reaction temperature constitutes a critical factor for chain initiation, propagation and termination in cationic polymerizations [117]. For isobutylene polymerizations, reaction rates tend to increase at lower temperatures [39,40,118], due to combination of thermodynamic (mainly solubilization and ionization effects) and kinetic reasons, turning the industrial process expensive and environmentally unsustainable due to the high demand for energy [22]. Besides, the low reaction temperatures can be needed to control the properties of the reaction product, given the characteristic extremely high rates of polymerization in these systems. This explains why C-PIB reactions have been mostly performed at very low temperatures (Figure 7) in scientific papers [31,96,108]. As a matter of fact, the lower temperatures favor the solvation of the active ions, causing the decrease in the rate of ion collapse, which impacts the final average molar masses of the products [37,75,96]. On the other hand, HR-PIB syntheses have been preferably conducted at relatively higher temperatures. Although higher temperatures contribute to production of materials with lower average molar masses [37,80], higher temperatures also lead to higher rates of β -proton abstraction, which leads to creation of exo vinyl bonds [37,116,118].

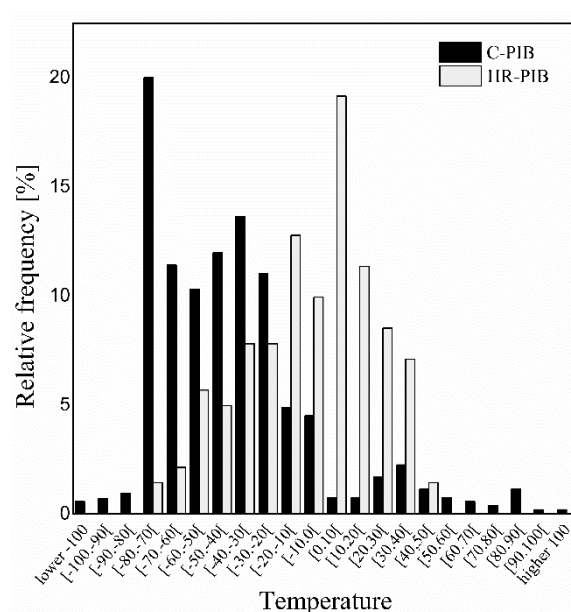


Figure 7. Frequencies of temperature citations in scientific papers related to C-PIB and HR-PIB manufacture.

As an important technological trend, studies are being developed to search for reaction systems that can be used to conduct isobutylene carbocationic reactions at temperatures that are close to room temperature in order to reduce the operation costs [42,62,71]. Particularly, some studies reported that manufacture of HR-PIB with AlCl_3 /ether using polar and non-polar solvents can be performed at temperature conditions that are close to room temperature (0 to 40 °C) and at short reaction times (below 30 min), leading to materials with high exo vinyl contents and better functionalization performances than industrially available HR-PIB grades [58,59,62,65].

3.1.6. Most Cited Papers

The downloaded papers were ranked in accordance with the total number of citations by other scientific publications, as shown in Table 7 for both C-PIB and HR-PIB products. As displayed in Table 7, the high citation frequencies of these papers in the last 2 decades indicate the persistent interest in these polymerization technologies.

Table 7. The 5 most cited papers in the field of cationic isobutylene polymerizations for production of C-PIB and HR-PIB.

Year of Publication	Total Number of Citations	Average Number of Citations per Year	Journal	JIF (2019)	SNIP (2019)	Year of Last Citation	Ref.
1987	229	6.65	<i>Journal of Polymer Science, Part A: Polymer Chemistry</i>	2.930	0.740	2021	[15]
1986	202	5.66	<i>Polymer Bulletin</i>	2.014	0.735	2021	[119]
1992	142	4.90	<i>Journal of Macromolecular Science—Part A: Pure and Applied Chemistry</i>	1.349	0.640	2020	[83]
1996	137	5.36	<i>Angewandte Chemie International</i>	12.959	2.254	2021	[120]
1996	117	4.88	<i>Macromolecules</i>	5.918	1.464	2018	[121]

Table 7. Cont.

Year of Publication	Total Number of Citations	Average Number of Citations per Year	Journal	JIF (2019)	SNIP (2019)	Year of Last Citation	Ref.
2010	67	6.00	<i>Macromolecules</i>	5.918	1.464	2020	[25]
2011	56	5.50	<i>Macromolecules</i>	5.918	1.464	2021	[107]
2010	56	5.00	<i>Polymer</i>	4.231	1.255	2021	[59]
2006	55	3.60	<i>Macromolecules</i>	5.918	1.464	2020	[85]
2012	51	5.56	<i>Journal of Polymer Science, Part A: Polymer Chemistry</i>	2.930	0.740	2021	[43]

For the C-PIB technology, the most influential papers were published in the late 1980s and early 1990s. Faust and Kennedy (1986 and 1987) presented comprehensive studies [15,119] about the effects of operation parameters on isobutylene carbocationic polymerizations with BCl_3 as catalyst and polar and non-polar solvents at low temperatures (-30°C), motivating discussions about the reaction mechanism and the modification of polymer chains of materials of commercial interest, which explains the interest arisen by these papers. Later, Gyor et al., 1992 (TiCl_4 /ether/mixture of polar and nonpolar solvents at extreme low temperatures) [83], Jacob et al., 1996 (TiCl_4 or BCl_3 /DtBP/polar or nonpolar solvents at extreme low temperatures) [121] and Bochmann and Dawson, 1996 (AlCl_3 /Tris(pentafluorophenyl)borane/polar solvents at extreme low temperatures) [120] discussed operation procedures to control the molar mass distributions, to reduce the dispersity and to enhance the functionalization efficiency the obtained polymer materials. As one can see, these papers provide information about the process operation conditions required to produce C-PIB materials with desired controlled properties.

The more contemporary literature regarding HR-PIB technologies focuses on improving the highly reactive behavior of the material through modification of the polymerization reaction conditions [25,43,59,66,85,107]. The complexity and high sensitivity of isobutylene polymerizations to changes of operation conditions challenge the production of HR-PIBs with specified properties. The success of these papers can be explained by the extremely promising results regarding the obtainment of high polymer yields, high exo vinyl contents and use of more convenient higher temperatures (above 0°C) for manufacture of HR-PIB, especially with AlCl_3 catalyst and hexane or chlorinated solvents, employing environmentally safer procedures and reagents and materials of lower costs.

3.2. Patents

After the data mining phase, the final set of downloaded documents comprised 203 published patents, including 66% patents related to C-PIB technologies and 34% papers related to HR-PIB technologies. As described for scientific papers, this scenario illustrates the more traditional use of C-PIB products and the largest commercial market of C-PIB materials, despite the growing market share of HR-PIB grades. The final set of documents included patents filed since the 1930s, which were analyzed in accordance with the categories described in Table 4 [57,66,122–301].

3.2.1. Yearly Distribution

Figure 8 presents the annual distribution of patents in the field of cationic isobutylene polymerizations, which were grouped into three categories (active, pending and not active), based on their current status at data acquisition date.

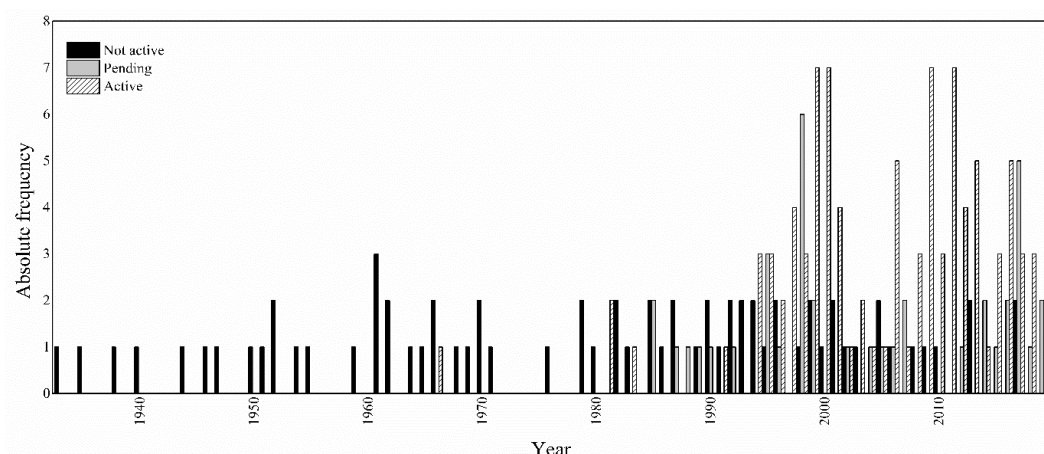


Figure 8. Number of patents in the field of PIB manufacture over the years [57,66,122–301].

As displayed in Figure 8, the number of patents published annually has grown since the 1990s, although the annual frequencies are relatively small. The oldest patent found in the search was published in 1933 by BASF SE (former IG Farben), regarding the polymerization of isobutylene using BF_3 and AlCl_3 as co-initiator and water as initiator [292]. Compared to the first patent related to the production of HR-PIB, which was published in 1990 by Zeon Co [290], there is a gap of almost 60 years between the first accepted C-PIB and HR-PIB patents. Quantitatively, among the 203 analyzed patents, 35% were withdrawn or expired, 46% were still active and 19% were under analysis, which can be regarded as a very significant number because of the analyzed time period and highlights the continuing interest in the technological development in this field. Nevertheless, comparing Figure 2 to Figure 8, similar trends can be observed, with fast growth of the number of documents after publication of the first patent about HR-PIB in 1990, and slow decrease in the number of documents in the 2010–2020 decade, indicating that the available technologies are mature and that new breakthroughs are needed to encourage innovative developments in this area.

It must be noted that the discussions presented in the next sections consider only active and pending patents, since the technologies proposed by expired patents are no longer protected and may be of no significant commercial interest anymore.

3.2.2. Distribution of Countries

Figure 9 and Table 8 show the distributions of active, pending and priority patents related to C-PIB and HR-PIB products in terms of the country of origin. In patents that are active in more than one country, the first filing was classified as the priority patent. Patents that have priority represent countries where the technology was developed and consequently companies that perform priority operations in the field. Patents regarding C-PIB manufacture have been filed primarily in 10 countries, mostly individually, although some of them have been deposited at European and worldwide offices. On the other hand, patents regarding HR-PIB manufacture have been filed in only 8 countries individually, although some of them have also been deposited at European and worldwide offices. It is important to note that the most recent patents have been deposited primarily in offices that represent several countries simultaneously (as EPO and WIPO), instead of one country at a time. This could indicate the strategy to initially protect the technology in a globalized context and postpone the selection of the countries where the patent will remain active for longer periods of time.

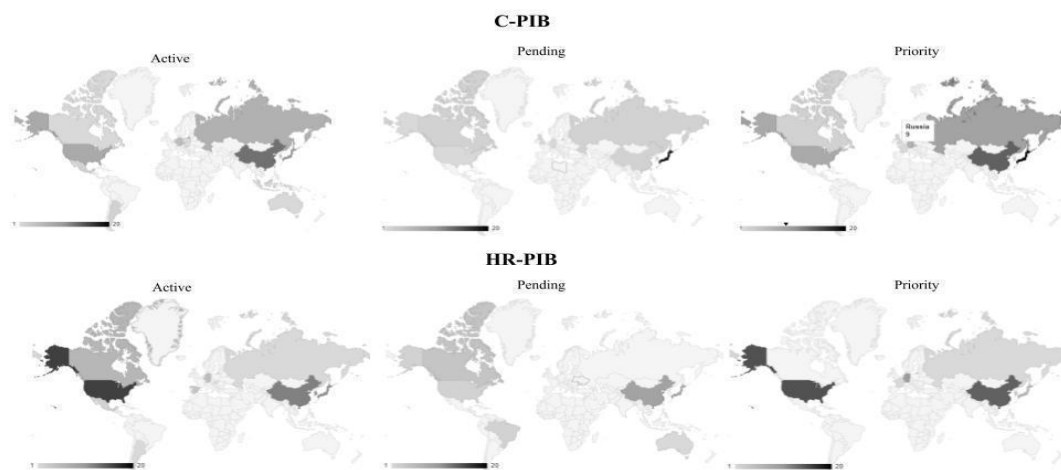


Figure 9. Distribution of patents regarding C-PIB and HR-PIB in terms of the country of origin, as a function of the current status [57,66,122–301].

Table 8. Distribution of patents regarding C-PIB and HR-PIB in terms of the country of origin, as a function of the current status [57,66,122–301].

C-PIB						
Active			Pending		Priority	
Ranking	Country	(%)	Country	(%)	Country	(%)
1	China	16.7	Japan	42.2	Japan	26.7
2	Japan	12.8	World	24.4	China	18.7
3	World	11.5	Europe	6.7	Russia	12.0
4	USA	10.3	Canada	4.4	USA	10.7
5	Russia	9.0	China	4.4	Germany	9.3
6	Germany	6.4	Russia	4.4	Europe	8.0
7	Czech Republic	5.1	Germany	2.2	Czech Republic	6.7
8	South Korea	3.9	USA	2.2	Canada	2.7
HR-PIB						
Active			Pending		Priority	
Ranking	Country	(%)	Country	(%)	Country	(%)
1	USA	18.2	World	24.4	USA	26.3
2	China	13.6	China	22.0	China	24.6
3	Japan	12.5	Japan	19.5	Germany	17.5
4	South Korea	11.4	Europe	12.2	Japan	10.5
5	World	11.4	Canada	9.8	Europe	7.0
6	Europe	10.2	Brazil	4.9	South Korea	5.3
7	Canada	6.8	USA	4.9	World	3.5
8	Germany	5.7	Australia	2.4	Russia	1.8

The development of PIB technologies is highly concentrated in the USA, China, Japan, Russia, and Germany, which represent almost 80% of all the active and pending filed patents (Table 8). This pattern is similar to the one observed for academic articles, although it is possible to note a growing incidence of active and pending patents deposited in China and through the World Intellectual Property Organization (WIPO), reinforcing the previously discussed trend for development of PIB technologies.

3.2.3. Patent Applicants and Players

Table 9 shows the companies and research centers that filed the analyzed patents. The patents regarding C-PIB technologies involved 25 institutions of 10 countries, while the patents regarding HR-PIB technologies involved 16 institutions of 8 countries. Kaneka Co. (Japan), BASF SE (Germany) and Otkrytoe Aktsionernoe Obshches (Russia) are the three top applicants for C-PIB patents, while BASF SE (Germany), Beijing University of Chemical Technology (China) and TPC Group (USA) are the top applicants for HR-PIB patents. It must be observed the main players in the PIB market are the TPC Group, Infineum, Lubrizol [246], BASF SE, INEOS (British Petroleum sold petrochemical business to INEOS in 2020) [302], Kaneka and Daelim. Based on this list, it can be observed that most of the main players are also among the main technology developers, as shown in Table 9 [219].

Table 9. Distribution of patents regarding C-PIB and HR-PIB in terms of the patent applicants [57,66,122–301].

C-PIB				
Ranking	Applicants	Country	Total Publications	(%)
1	Kaneka Co.	Japan	18	27
2	BASF SE	Germany	11	16
3	Otkrytoe Aktsionernoe Obshches	Russia	5	7
4	Arlanxeo	Saudi Arabia	4	6
5	British Petroleum	United Kingdom	3	4
6	Bridgestone	Japan	2	3
6	China National Petroleum Co.	China	2	3
6	Czech Academy of Sciences	Czech Republic	2	3
6	Dandong Mingzhu Special Type Resin Co.	China	2	3
6	The University of Akron	USA	2	3
6	TPC Group	USA	2	3
HR-PIB				
Ranking	Applicants	Country	Total Publications	(%)
1	BASF SE	Germany	17	32
2	Beijing University of Chemical Technology	China	7	13
2	TPC Group	USA	7	13
3	Infineum	United Kingdom	6	11
4	Daelim	South Korea	3	6
5	China National Petroleum Co.	China	2	4
5	Petrochemicals Co.	Japan	2	4

3.2.4. Operation Parameters for Isobutylene Polymerizations

The main operation parameters reported in the published patents were analyzed and the most significant ones were grouped for each technology (C-PIB or HR-PIB), as performed previously for scientific papers.

Lewis Acid Catalysts

Figure 10 shows the frequencies of catalyst citations in published patents. Among the active patents, some catalysts were more widely used for manufacture of C-PIB, such as TiCl_4 and SnCl_4 , some catalysts were related more specifically to production of HR-PIB, such as AlBr_3 and triethylamine (TEA), and some others, including BuAlCl_2 , BF_3 , AlCl_3 , FeCl_3 and ZnCl_2 , were mentioned equally for manufacture of C-PIB and HR-PIB.

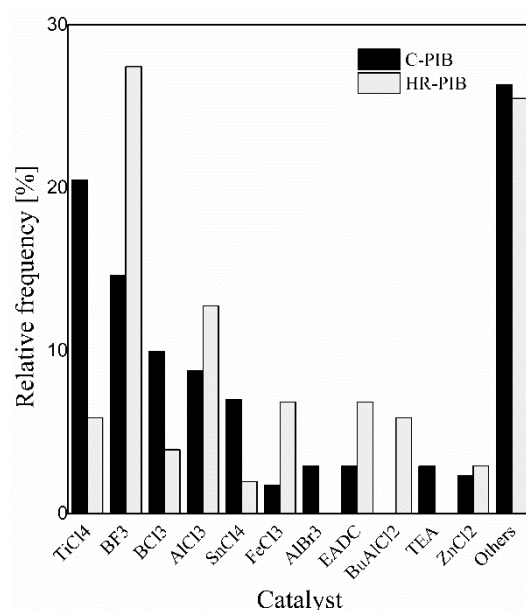


Figure 10. Frequencies of catalyst citations in patents related to C-PIB and HR-PIB manufacture. (EADC: Ethylaluminum dichloride).

Regarding HR-PIB, BF₃ was the catalyst reported most frequently (27.5%), confirming the relevance of the BF₃ catalyst in the industrial environment and reinforcing the interpretation that the relatively small number of academic investigations related to BF₃ is due to safety issues and difficult handling of this chemical compound. This result also agrees well with the evolution of the HR-PIB technology, as BASF SE patented the process to produce HR-PIB with high monomer conversions (around 95%), average molar masses between 500 and 5000 Da and more than 90% of exo vinyl groups with the BF₃ catalyst [22,95].

It is also worth mentioning the relatively high number of patents related to the use of the AlCl₃ catalyst for manufacture of HR-PIB, which reflects the continuous search for environmentally safer catalysts and operation at higher temperatures, as BF₃ processes are normally operated at exceptionally low reaction temperatures. It is also interesting to observe the very high relative number of patents involved with “Others” catalysts, indicating that the PIB business is still searching for new less expensive and environmentally safer catalysts for manufacture of both C-PIB and HR-PIB grades.

Lewis Base Co-Catalysts

Figure 11 presents the chemical functions used most often as co-catalysts for production of PIB grades. It is interesting to observe that 20% of the patents regarding C-PIB did not use any sort of co-catalyst to produce the polymer. When production of HR-PIB is concerned, the absence of the co-catalysts was less frequent (10%), indicating the importance of the co-catalyst to produce the exo vinyl double bond. As explained previously, this is supported by mechanistic interpretation of the chain transfer step, which must involve elimination of β-proton to generate the exo vinyl group [22]. Amines and silanes were reported as co-catalysts for C-PIB reactions only, while thiocompounds were used as cocatalysts to produce HR-PIB exclusively.

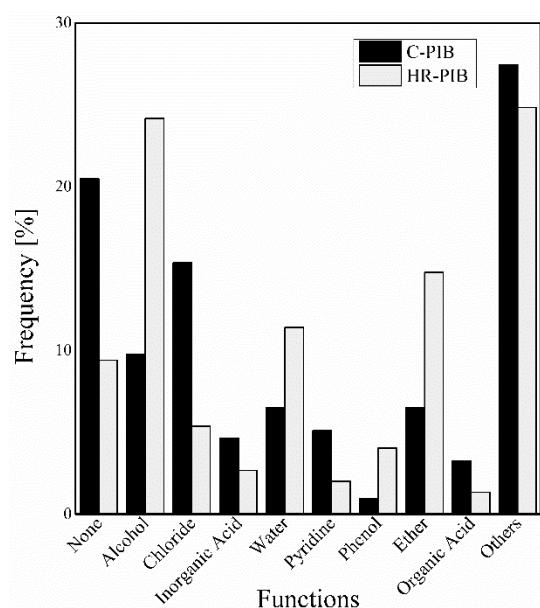


Figure 11. Frequencies of co-catalyst citations in patents related to C-PIB and HR-PIB manufacture.

Regarding the use of co-catalysts, data extracted from academic articles and patents differ significantly. For instance, academic studies investigated the use of different nitrogen compounds as co-catalysts, such as pyridine (22%), while only 5% of the patents reported the use of amines for this function. Besides, 30% of the co-catalysts reported by patents were classified as “Others” for C-PIB and 27% for HR-PIB, illustrating the intense search for new co-catalysts for PIB manufacture. Additionally, scientific papers described the use of ethers as co-catalysts in 40% of the publications regarding HR-PIB production (as one can see in Figure 5), while the preference among patents is for alcohols (22%, as shown in Figure 11). Once more, this reinforces the continuous efforts to use less hazardous and less expensive compounds in industrial environments, such as water and simple alcohols, over halides and nitrogen compounds.

Solvents

Figure 12 presents the solvents reported most often in patents related to cationic isobutylene polymerizations. As reported in the patents, numerous solvents have been used to produce C-PIB and HR-PIB. Hexane, toluene, dichloromethane, and chloromethane have been preferred for production of C-PIB, while hexane, chloromethane and the C4 mixture have been used most often for production of HR-PIB. The use of C4 mixtures illustrates the efforts to obtain a better added value product from a feedstock that is available in most chemical centers. However, academic articles and patents converge about the commonest solvents, as in both cases hexane and toluene (among nonpolar solvents) and dichloromethane and chloromethane (among the polar solvents) are the solvents used most frequently. Nevertheless, the group “Others” contributes significantly to the analyzed solvent scenario, illustrating once more in this case the intense search for new solvents for PIB manufacture.

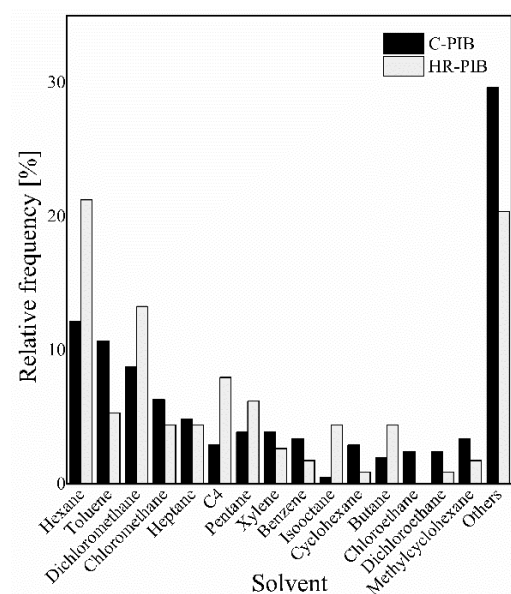


Figure 12. Frequencies of solvent citations in patents related to C-PIB and HR-PIB manufacture.

Temperatures

Figure 13 presents the reaction temperatures claimed in patent descriptions. As performed previously, the claimed temperature range was divided into intervals of 10 °C. It is important to mention that the range of temperatures that each patent aimed to protect was not necessarily the same used to perform the reaction trials in the examples. The most frequent range of temperatures used in C-PIB technologies was placed between -70 °C and $+50$ °C, which is an overly broad range. For HR-PIB, the claimed temperature range was narrower: between -20 °C and $+30$ °C. This extensive range of temperatures, 80 °C for C-PIB and 50 °C for HR-PIB, could be part of the intellectual protection strategy, once potential competitors would not be able to overcome the claimed process. When used for manufacture of engine oil/lubricant dispersants, PIBs with low average molar masses perform better. For this type of application, polymerizations performed at higher temperatures are essential for production of short polymer chains through chain transfer reactions [22].

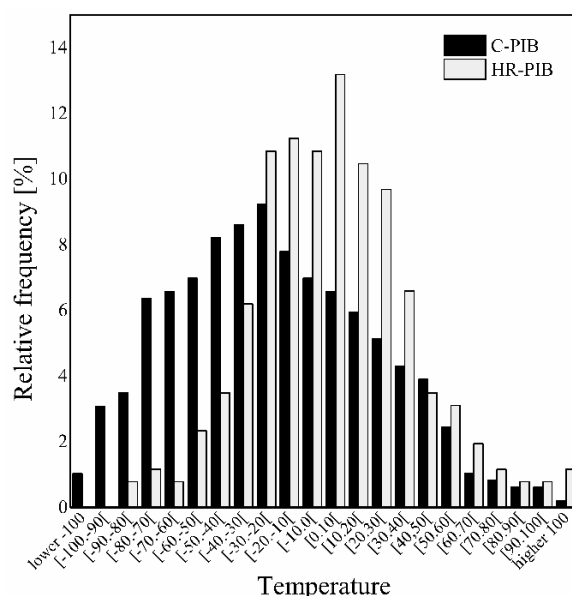


Figure 13. Frequencies of reported reaction temperatures in patents related to C-PIB and HR-PIB manufacture.

Although patent claims tend to protect very wide temperature ranges, scientific articles and patents converge to similar polymerization temperature ranges for C-PIB ($-70\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$) and for HR-PIB ($-20\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$). This once more indicates the efforts to produce PIBs with high exo vinyl contents at milder temperatures [22].

3.3. Correlation Analysis

To understand the effects of certain operating parameters on important properties of the final polymer material, standard principal component analysis (PCA) was conducted with operating parameters extracted from the bibliometric review [303]. The selected parameters were catalyst, cocatalyst, solvent, temperature, yield and vinyl content. Non-numeric variables were digitally normalized as shown in Table 10, considering the acidity (catalyst) and polarity (solvent and cocatalyst) of the analyzed species.

Table 10. Non-numeric normalized variables.

	0.00	0.25	0.50	1.00
Catalyst	AlCl_3		TiCl_4	BF_3
Solvent	DCM	DCM/Hexane (75/25)	Toluene	Hexane
Cocatalyst	Alcohol			Ether

PCA analyses were performed using STATISTICA[®] 10 software [303]. The data were initially normalized in accordance with Equation (1) and used as inputs for the analyses. Tables 11 and 12 show the eigenvalues, the eigenvectors (factors), the total variances (%), the cumulative eigenvalues and the cumulative variances (%).

$$Z = \frac{(\text{value} - \text{average})}{\text{standard deviation}} \quad (1)$$

Table 11. Eigenvectors and variabilities of the principal components.

Factors	Eigenvalue	Total Variance (%)	Cumulative Eigenvalue	Cumulative Variance (%)
Factor 1	1.964	32.7	1.96	32.7
Factor 2	1.129	18.8	3.09	51.6
Factor 3	1.034	17.2	4.13	68.8
Factor 4	0.947	15.8	5.08	84.6
Factor 5	0.632	10.5	5.71	95.1
Factor 6	0.294	4.9	6.00	100

Table 12. Eigenvectors associated with the principal components.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Catalyst	−0.844	0.204	−0.0797	0.298	−0.091	0.379
Cocatalyst	0.715	0.266	0.0487	0.100	−0.628	0.110
Solvent	−0.407	0.750	−0.430	−0.129	−0.098	−0.246
Temperature	0.416	0.197	−0.116	0.839	0.256	−0.072
Yield	−0.568	−0.041	0.694	0.278	−0.245	−0.237
Vinyl	−0.282	−0.0643	−0.587	0.225	−0.308	−0.128

Table 11 shows that Factor 1, the largest one, explains only 32.7% of the data variability, while Factor 2, the second largest one, explains only 18.8% of the variability. The cumulative variance for the first two factors is therefore equal to only 51.6%. As a matter of fact, it is necessary to consider five factors simultaneously to reach the cumulative variability of 95%, indicating that the analyzed conditions present high variability and that the analyzed variables tend to vary independently, so that very heterogeneous combinations of all analyzed variables should be expected in the data set.

Table 12 presents the values of the individual components of the eigenvectors, which indicate the observed correlations among the analyzed variables along the principal directions. One can see that the first direction describes variations of the catalyst systems, which tend to combine AlCl_3 with ethers and BF_3 with alcohols (explaining the opposite signs). This probably reflects the continuous search for new catalyst systems and the current industrial activity in the field. The second factor concentrates solvent variations, while factor 3 describes polymer product changes and factor 4 describes temperature changes. Although the observed component values of vinyl contents are generally small and not significant, they seem to be inversely correlated with the yield values in factor 3 (the one that describes product changes), which should be considered during mechanistic studies.

The covariance matrices of available data were calculated with help of different factor rotation functions, which are used to maximize the correlations among the measured variables and the factors calculated by the PCA [303]. However, in all cases the covariance values were not significant. This result indicates that quantitative analyses of variable fluctuations depend on multiple disturbances and possibly respond nonlinearly to modification of process operation conditions. From a practical point of view, this also indicates that it is not possible to determine how the exo vinyl content of obtained PIB products depend on observed process variables through standard multivariate linear analyses. This might already be expected, as HR-PIB products can be obtained with distinct catalyst systems, solvents, and operation conditions, as described throughout this manuscript, imposing the careful optimization of the particularly analyzed reaction system whenever maximization of the exo vinyl content of the final resin is sought.

Finally, it is important to note that during the writing of the present document no significant change of the article publication and of the patent filing scenarios was observed in the field of polyisobutylene manufacture. For this reason, the main trends and perspectives presented here and discussed in the previous sections are not constrained by the dates of publication of the utilized references and can be regarded as synchronized with the disclosure of the present study.

4. Conclusions

Polyisobutylenes (PIBs) constitute a very versatile family of polymer materials that has arisen growing industrial interest and stimulated the continuous growth of the PIB market size. Particularly, PIBs are produced commercially through cationic polymerization mechanisms, which are characterized by high reactivity and high sensitivity to changes of operation conditions, demanding operation in controlled environments and very peculiar sets of reaction conditions. Consequently, there has been continuous search for more efficient, less expensive, and environmentally friendly and safer production methodologies both in academia and in industrial environments.

Broadly speaking, PIBs are grouped commercially into two large families of products: conventional PIBs (or C-PIBs) and highly reactive PIBs (or HR-PIBs), depending on the contents of unsaturated terminal double bonds of polymer chains (exo vinyl content). HR-PIB materials contain high amounts of exo vinyl groups (>70%) and allow much easier functionalization for manufacture of oil and lubricant additives.

The proposed bibliometric survey on isobutylene cationic polymerization allowed for the first time the investigation of extensive scientific data published in the form of research papers (dating from 1949 to 2020) and in the form of deposited patents (dating from 1933

to 2020), which provided an updated and comprehensive literature review on the theme and quantitative measures of technological trends.

Academic investigations focused mostly on C-PIB materials, although the number of investigations regarding HR-PIB products has increased steadily, revealing the growing commercial importance and ever-increasing maturity of this technology. Consequently, the vast majority of scientific publications in this field is concentrated in developed countries, where the main commercial players of PIB materials are located. In particular, the main focus of academic works has been the interpretation of the mechanism of polymerization and the adjustment of operation conditions for manufacture of C-PIB and HR-PIB grades with controllable properties, using mild reaction temperatures and alternative catalyst systems. The development of more appropriate catalyst systems still constitutes a significant challenge in the field, since the successful stabilization of the carbocation, and consequently the success of the polymerization, is the result of complex synergetic interactions that involve thermodynamic and kinetic effects, reflected on the characteristics of the solvent, of the Lewis acid catalyst, of the Lewis base co-catalyst and on the reaction temperature.

When patents are analyzed and compared to scientific publications, similar trends can be observed, although the variabilities of reported solvents, Lewis acid catalysts and Lewis base co-catalysts are higher (reflecting the continuous search for more appropriate catalysts and solvents); the reported use of the BF_3 catalyst is more frequent (reflecting the fact that safety and handling issues prevent the use of the BF_3 catalyst in academic environments); and the use of less expensive co-catalysts (such as organic alcohols and water) is commoner.

Finally, based on the performed survey, it seems appropriate to say that efforts are being made to develop operation strategies to obtain PIB grades with low dispersities, controlled average molar masses and high exo vinyl contents with high monomer conversions, using mild reaction temperatures (0 to 40 °C) and environmentally friendly and safer solvents and catalyst systems (involving more frequently the AlCl_3 catalyst and ethers as co-catalysts).

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