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REVIEW OF RECENT ADVANCES IN POLYCARBONATE SYNTHESIS

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Abstract. Recent advances in polycarbonate synthesis have been driven by the urgent need for sustainable alternatives to petroleum-based polymers and effective strategies for carbon dioxide utilization. This review examines the latest developments in polycarbonate synthesis, encompassing bio-based feedstocks, innovative catalytic systems, and circular economy approaches. Key topics include the synthesis of bio-based polycarbonates from renewable resources such as isosorbide and terpenes, the copolymerization of CO_2 with various epoxides, and the development of functionalized polycarbonates with tailored properties. Novel catalytic systems—including ionic liquids, metal-organic complexes, and metal-free catalysts—are critically analyzed for their efficiency, selectivity, and environmental impact. The review also explores advanced synthetic methodologies such as melt chain extension, one-pot synthesis approaches, and reversible polycondensation techniques that enable precise control over molecular weight and end-group functionality. Particular attention is given to chemical recycling strategies that enable closed-loop material lifecycles, including the upcycling of polycarbonate waste and spent lithium battery electrolytes into valuable polymer products. Applications of these advanced polycarbonates span diverse fields including low-dielectric materials for electronics, flame-retardant materials with enhanced safety profiles, biomedical materials, and thermal insulation foams. Structure-property relationships are systematically examined to understand how monomer selection, polymer architecture, and functional group incorporation influence thermal stability, mechanical properties, optical characteristics, and processability. The integration of sustainability principles with high-performance material design represents a paradigm shift toward environmentally responsible polymer production that simultaneously addresses plastic waste management, carbon emissions reduction, and resource conservation.

Keywords: polycarbonate synthesis; bio-based polymers; CO_2 utilization; chemical recycling; catalytic systems; sustainable materials; circular economy

Аннотация. Последние достижения в области синтеза поликарбонатов обусловлены острой необходимостью разработки устойчивых альтернатив полимерам нефтяного происхождения, а также эффективных стратегий утилизации диоксида углерода. В настоящем обзоре рассматриваются современные направления синтеза поликарбонатов, охватывающие

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использование биооснованного сырья, инновационных каталитических систем и подходов циркулярной экономики. Ключевые аспекты включают синтез биооснованных поликарбонатов из возобновляемых ресурсов, таких как изосорбид и терпены, сополимеризацию CO_2 с различными эпоксидами, а также разработку функционализированных поликарбонатов с заданными свойствами. Новые каталитические системы, включая ионные жидкости, металлоорганические комплексы и безметалльные катализаторы, подвергнуты критическому анализу с точки зрения их эффективности, селективности и экологического воздействия. В обзоре также рассматриваются передовые синтетические методологии, такие как удлинение цепей в расплаве, одностадийные (one-pot) методы синтеза и обратимые процессы поликонденсации, обеспечивающие точный контроль молекулярной массы и функциональности концевых групп. Особое внимание уделяется стратегиям химической переработки, направленным на создание замкнутых материальных циклов, включая апсайклинг отходов поликарбонатов и отработанных электролитов литий-ионных аккумуляторов с получением ценных полимерных продуктов. Области применения полученных поликарбонатов охватывают низкодиэлектрические материалы для электроники, огнезащитные материалы с повышенными показателями безопасности, биомедицинские материалы и теплоизоляционные пены. Систематически анализируются взаимосвязи «структура — свойства», позволяющие установить влияние выбора мономеров, архитектуры полимерной цепи и введения функциональных групп на термическую стабильность, механические характеристики, оптические свойства и перерабатываемость материалов. Интеграция принципов устойчивого развития с проектированием высокоэффективных материалов рассматривается как парадигмальный переход к экологически ответственному производству поликарбонатов, одновременно решающий задачи управления пластиковыми отходами, сокращения выбросов углерода и рационального использования ресурсов.

Ключевые слова: синтез поликарбонатов; биооснованные полимеры; утилизация CO_2; химическая переработка; каталитические системы; устойчивые материалы; циркулярная экономика

Annotatsiya. Polikarbonatlarni sintez qilish sohasidagi so‘nggi yutuqlar neft asosidagi polimerlarga barqaror muqobillar yaratish zarurati hamda karbonat angidridni samarali utilizatsiya qilish strategiyalariga bo‘lgan ehtiyoj bilan bog‘liq. Ushbu sharh maqolada polikarbonatlar sintezining zamonaviy yo‘nalishlari, jumladan bioasosli xomashyo manbalari, innovatsion katalitik tizimlar va aylanuvchi (sirkulyar) iqtisodiyotga asoslangan yondashuvlar keng yoritilgan.

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Asosiy masalalar qatoriga izosorbid va terpenlar kabi qayta tiklanuvchi resurslardan bioasosli polikarbonatlarni olish, CO_2 ning turli epoksidlar bilan sopolimerizatsiyasi hamda belgilangan xossalarga ega funksional polikarbonatlarni ishlab chiqish kiradi. Ion suyuqliklar, metall-organik komplekslar va metalsiz katalizatorlarni o‘z ichiga olgan yangi katalitik tizimlar ularning samaradorligi, selektivligi va ekologik ta’siri nuqtayi nazaridan tanqidiy tahlil qilinadi. Shuningdek, eritmada zanjirni uzaytirish, bir bosqichli sintez usullari va qaytar polikondensatsiya jarayonlari kabi ilg‘or sintetik metodologiyalar ko‘rib chiqilib, ular molekulyar massa va uchki guruhlar funksionalligini aniq nazorat qilish imkoniyatini berishi ta’kidlanadi. Yopiq material aylanishini ta’minlovchi kimyoviy qayta ishlash strategiyalariga, jumladan polikarbonat chiqindilari hamda ishlatilgan litiy-ion batareyalar elektrolitlarini yuqori qiymatli polimer mahsulotlariga aylantirish jarayonlariga alohida e’tibor qaratilgan. Ushbu ilg‘or polikarbonatlarning qo‘llanish sohalari elektronika uchun past dielektrik materiallar, yuqori xavfsizlik ko‘rsatkichlariga ega olovbardosh materiallar, biotibbiyot materiallari va issiqlik izolyatsion ko‘piklarni o‘z ichiga oladi. «Tuzilma — xossa» o‘zaro bog‘liqliklari tizimli ravishda tahlil qilinib, monomer tanlovi, polimer zanjiri arxitekturasi va funksional guruhlarning kiritilishi natijasida termik barqarorlik, mexanik xossalar, optik xususiyatlar hamda qayta ishlanuvchanlikka ko‘rsatadigan ta’siri aniqlanadi. Barqarorlik tamoyillarini yuqori samarali materiallar dizayni bilan integratsiyalash polikarbonatlar ishlab chiqarishda ekologik mas’uliyatli yondashuvga o‘tishning muhim yo‘li sifatida qaralib, plastik chiqindilarni boshqarish, uglerod chiqindilarini kamaytirish va resurslardan oqilona foydalanish muammolarini bir vaqtning o‘zida hal etishga xizmat qiladi.

Kalit so‘zlar: polikarbonatlar sintezi; bioasosli polimerlar; CO_2 utilizatsiyasi; kimyoviy qayta ishlash; katalitik tizimlar; barqaror materiallar; aylanuvchi iqtisodiyot

Introduction

The global polymer industry stands at a critical juncture, facing mounting pressures from plastic pollution, fossil resource depletion, and climate change imperatives. Polycarbonates, a class of engineering thermoplastics characterized by carbonate linkages (-O-CO-O-) in their polymer backbone, have long been valued for their exceptional combination of optical clarity, impact resistance, thermal stability, and dimensional stability [1]. Conventional polycarbonates, particularly bisphenol A polycarbonate (BPA-PC), have found widespread applications in automotive components, electronic devices, medical equipment, construction materials, and consumer products. However, the traditional production of polycarbonates relies heavily on petroleum-derived monomers and

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phosgene-based chemistry, raising significant environmental and health concerns that have catalyzed the search for more sustainable alternatives.

The transition toward sustainable polycarbonate production encompasses multiple strategic directions: the utilization of renewable bio-based feedstocks, the incorporation of carbon dioxide as a C1 building block, the development of environmentally benign catalytic systems, and the implementation of circular economy principles through chemical recycling [1, 11]. Bio-based monomers derived from plant oils, terpenes, lignocellulosic biomass, and industrial byproducts offer the potential to reduce dependence on fossil resources while maintaining or even enhancing material performance [12]. Simultaneously, the copolymerization of CO_2 with epoxides represents a dual benefit: the chemical fixation of a greenhouse gas and the production of polycarbonates with tunable properties [4, 13]. These approaches align with global sustainability goals and the growing demand for carbon-neutral or carbon-negative materials.

Recent years have witnessed remarkable progress in catalyst design, with innovations spanning homogeneous metal complexes, heterogeneous catalysts, metal-free organocatalysts, and ionic liquid-based systems [7, 10, 11]. These catalytic advances have enabled greater control over polymerization kinetics, molecular weight distribution, polymer microstructure, and functional group incorporation. Furthermore, the development of sophisticated synthetic methodologies—including one-pot synthesis, melt chain extension, and reversible polycondensation—has improved process efficiency and expanded the accessible range of polymer architectures [2, 6, 8]. The ability to precisely control polymer structure has direct implications for tailoring material properties to meet specific application requirements, from low-dielectric materials for high-frequency electronics to flame-retardant polymers for safety-critical applications [8, 15].

Beyond synthesis, the end-of-life management of polycarbonates has emerged as a critical consideration in sustainable material design. Chemical recycling approaches that depolymerize polycarbonates back to their constituent monomers enable truly circular material lifecycles, in contrast to mechanical recycling which often results in progressive property degradation [3, 8, 12]. Moreover, innovative upcycling strategies have demonstrated the potential to transform polycarbonate waste and even unrelated waste streams, such as spent lithium battery electrolytes, into valuable polymer products [3, 5]. These developments collectively represent a paradigm shift from linear "take-make-dispose" models to circular systems that minimize waste, conserve resources, and reduce environmental impact.

This review synthesizes recent advances in polycarbonate synthesis, with emphasis on sustainable feedstocks, innovative catalytic systems, synthetic

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methodologies, structure-property relationships, and circular economy approaches. By examining the state-of-the-art across these interconnected areas, we aim to provide a comprehensive understanding of current capabilities and identify opportunities for future research and development toward truly sustainable polycarbonate materials.

Literature review

The synthesis of sustainable bio-based polycarbonates has emerged as a critical research frontier in addressing the dual challenges of plastic pollution and carbon emissions. Recent developments have focused on utilizing renewable feedstocks and carbon dioxide as raw materials for polycarbonate production. A comprehensive examination of bio-based polycarbonates reveals that the copolymerization of CO_2 with renewable epoxides derived from diverse sources—including plant oils, terpenes, lignocellulosic biomass, and industrial byproducts—offers a promising pathway toward carbon-neutral materials. The integration of various catalytic systems, both heterogeneous and homogeneous, has been shown to significantly influence polymerization efficiency and selectivity. Furthermore, the structural characteristics of epoxide monomers directly impact the thermal, mechanical, and optical properties of the resulting polymers, while post-polymerization modifications enable tailored functionality for specific applications ranging from coatings and adhesives to biomedical materials. The successful implementation of these technologies requires continued advancement in catalyst design, integration of artificial intelligence in manufacturing processes, and supportive policy frameworks to enable economically viable and environmentally sustainable production at industrial scales [1].

Isosorbide-based polycarbonates represent a particularly attractive class of bio-derived materials due to their renewable origin and potential to replace petroleum-based alternatives. Traditional melt-transesterification polycondensation methods for synthesizing modified isosorbide polycarbonates have been constrained by the necessity of high reaction temperatures and prolonged reaction times, which often result in molecular weight degradation and undesirable color changes in the final product. A novel approach utilizing melt chain extension methodology with polyethylene glycol (PEG) modification has demonstrated significant advantages in addressing these limitations. This method enables the synthesis of isosorbide-based copolycarbonates (PEXHDCYC) with weight-average molecular weights ranging from 19,004 to 73,294 g/mol under milder conditions and shorter reaction times. Notably, the incorporation of PEG1000 allows for systematic tuning of the glass transition temperature, with Tg decreasing as PEG content increases. The resulting materials exhibit exceptional mechanical properties, including an impressive elongation at break of up to 135.45% ± 24%,

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while maintaining superior optical characteristics compared to conventional bisphenol A polycarbonate (BPA-PC). These improvements in processability, molecular weight control, and material properties position this synthetic strategy as a viable route for commercial production of high-performance bio-based polycarbonates [2].

The circular economy approach to polymer waste management has gained considerable momentum through chemical upcycling strategies that convert end-of-life plastics into valuable materials. A particularly innovative example involves the transformation of bisphenol A polycarbonate waste into Mannich polyols through a streamlined one-pot process. This methodology combines two consecutive reactions—methanolysis-based depolymerization of BPA-PC followed by Mannich polyol synthesis—within a single vessel without requiring intermediate purification steps, thereby significantly enhancing process efficiency and reducing solvent consumption. The resulting Mannich polyols serve as effective building blocks for producing rigid polyurethane foams with highly desirable properties for thermal insulation applications. These foams exhibit low density, a predominantly closed-cell morphology, and exceptional thermal conductivity values as low as 23.3 $mW \cdot m^{-1} \cdot K^{-1}$. This approach not only provides a practical solution for managing plastic waste but also creates new-generation materials with incorporated recycled content, contributing to both carbon footprint reduction and the mitigation of environmental challenges associated with plastic accumulation [3].

The development of functionalized polycarbonates through CO_2 fixation has opened new avenues for creating materials with tailored properties suitable for high-performance applications. A significant advancement in this area involves the design of a binary catalytic system comprising a novel trinuclear tetradentate Schiff base chromium complex combined with bis(triphenylphosphine) imidazolium salt (PPNN3). This catalytic system facilitates the one-step copolymerization of CO_2 with bicyclic epoxide compounds containing both terminal and internal epoxy groups (VCHDEP), yielding bifunctional polycarbonates (PVCH) with a unique architecture. The resulting polymers feature a polycarbonate cyclohexene ester backbone with side chains containing both epoxy and cyclic carbonate functional groups, with the EP/CC ratio being precisely controllable through manipulation of reaction temperature and PPNN3 molar ratio. Remarkably, PVCH exhibits a glass transition temperature of 164.5 °C, surpassing that of conventional BPA-based polycarbonates (154 °C), indicating enhanced thermal stability and mechanical robustness. The catalytic system demonstrates high selectivity for ring-opening copolymerization of epoxides to form the polymer backbone while preserving unreacted epoxy groups in the side chains. Thermodynamic analysis reveals an

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enthalpy change ($\Delta H°_p$) of -20.5 kJ mol^{-1}, entropy change ($\Delta S°_p$) of -80.3 J mol^{-1} K^{-1}, Gibbs free energy change ($\Delta G°_p$) of 3.5 kJ mol^{-1}, and activation energy (E_a) of 56.8 kJ/mol for the polymerization process. The retained functional groups enable further chemical modifications through hydrolysis and amination reactions, producing polycarbonates with hydroxyl, amide, and other functional groups that enhance adhesion, biocompatibility, and chemical reactivity for advanced material applications [4].

The valorization of spent lithium-ion batteries represents both an environmental imperative and an economic opportunity, as the accumulation of battery waste poses significant disposal challenges while containing valuable chemical components. A novel approach to addressing this challenge involves the synthesis of high-value copolycarbonates from spent lithium battery electrolytes in combination with renewable monomers. Using 1,3-(p-toluic acid zinc salt)Im $ZnCl_3$ as a catalyst, researchers have successfully synthesized a series of copolycarbonates incorporating isosorbide (ISB), bisphenol A (BPA), and components from spent lithium-ion batteries (s-LIBs). This catalytic system enables the production of high molecular weight copolycarbonates (PIBs) with weight-average molecular weights ranging from 57,000 to 110,000 g mol^{-1}. The strategic incorporation of thermally stable and flexible ISB units into the polymer backbone enhances the thermal stability of the resulting copolycarbonates while simultaneously improving polymer chain flexibility. This dual improvement addresses a critical limitation of conventional BPA polycarbonates, which are known for their inherent brittleness. The successful integration of battery waste components into polymer structures not only provides a sustainable disposal pathway for s-LIBs but also demonstrates the potential for developing environmentally friendly soft polycarbonates with enhanced mechanical properties, contributing to both green chemistry principles and circular economy objectives [5].

Telechelic polymers, characterized by well-defined functional end groups, are valuable building blocks for advanced polymer architectures and materials with controlled properties. A significant challenge in their synthesis has been the elimination of cyclic polymer byproducts, which can compromise material performance. A novel approach utilizing reversible polycondensation through alkoxide exchange reactions has demonstrated the efficient synthesis of linear telechelic polycarbonates free from cyclic polymers. This methodology employs the polycondensation of diol formate with dipropyl carbonate under reduced pressure in the presence of 5 mol% potassium tert-butoxide (tBuOK) as an alkoxide exchange catalyst, with careful control of reagent stoichiometry. When using excess dipropyl carbonate, linear polycarbonates with propyl carbonate moieties at

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both ends are obtained, with number-average molecular weight (M_n) reaching 6,510 g/mol when the carbonate excess is reduced to 1.10 equivalents. Conversely, polycondensation using excess diol formate in bulk yields linear polycarbonates with hydroxyl groups at both termini, achieving M_n values up to 10,100 g/mol with 1.04 equivalents of diol formate. The methodology's versatility is further demonstrated through the incorporation of functional carbonates or functional diol esters during equimolar polycondensation, enabling the synthesis of telechelic polycarbonates with diverse functional groups at both chain ends. This simple yet effective approach provides a robust platform for creating well-defined polymer architectures with precise end-group functionality, essential for applications in block copolymer synthesis, surface modification, and functional material design [6].

The development of effective catalytic systems for polyester and polycarbonate synthesis has been significantly advanced through the design of zirconium-based coordination complexes. A systematic investigation of both mononuclear and dinuclear tetravalent zirconium compounds, synthesized from Schiff base proligands and zirconium alkoxide reagents, has revealed distinct structural and catalytic characteristics. Dimeric isopropoxide Zr(IV) complexes feature two zirconium centers connected through bridging isopropoxide groups, with each metal center adopting a distorted octahedral geometry. These dimeric species demonstrate catalytic activity for the ring-opening polymerization (ROP) of rac-lactide but exhibit negligible activity for the ring-opening copolymerization (ROCOP) of cyclohexene oxide with CO_2. In contrast, monomeric tert-butoxide Zr(IV) compounds, in which the zirconium center possesses a coordination number of five, display significantly broader catalytic versatility. These mononuclear complexes effectively catalyze both ROP and ROCOP reactions, producing both polyesters and aliphatic polycarbonates. Notably, the mononuclear compounds achieve greater than 99% carbonate linkage in the polycarbonate chain, demonstrating exceptional selectivity for carbonate formation over ether linkages. This structure-activity relationship study provides valuable insights into catalyst design principles, highlighting how metal coordination environment and nuclearity directly influence catalytic performance and product selectivity in polymerization reactions [7].

The development of high-performance polycarbonates that simultaneously address mechanical robustness, fire safety, and end-of-life recyclability represents a significant challenge in polymer science. A breakthrough approach involves the one-pot green synthesis of liquid crystalline polycarbonate (LCPC) through facile melt polycondensation, incorporating liquid crystalline structures in situ. This innovative design strategy yields materials with exceptional mechanical properties,

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including a 32% improvement in tensile strength and an impact strength of approximately 40 kJ m^{-2}, positioning LCPC among the highest-performing flame-retardant polycarbonate materials reported to date. Beyond mechanical excellence, LCPC demonstrates outstanding fire safety characteristics, achieving a UL-94 V-0 rating at a thickness of merely 0.4 mm and a limiting oxygen index of 44.9%. Compared to conventional polycarbonate materials, LCPC exhibits remarkable reductions of 62.7% in peak heat release rate and 77.3% in total smoke release, addressing critical safety concerns in applications requiring flame resistance. Perhaps most significantly, LCPC demonstrates efficient closed-loop chemical recyclability, as it can be depolymerized into its constituent monomers under mild conditions. The recovered monomers can be repolymerized to produce materials with performance characteristics comparable to the virgin polymer, establishing a truly circular material lifecycle. This integrated approach to material design—combining enhanced performance with inherent recyclability—provides a sustainable pathway for developing multifunctional polymeric materials that meet both application requirements and environmental imperatives [8].

Understanding the kinetics and mechanisms of polycarbonate synthesis is essential for optimizing industrial production processes and achieving consistent product quality. A comprehensive kinetic modeling study of 4,4-(hexafluoro-isopropyl)diphenol (BPAF) polycarbonate synthesis via melt transesterification has provided valuable insights into both catalytic and non-catalytic reaction pathways. This research addresses the condensation and polymerization reactions between BPAF and diphenyl carbonate (DPC), developing a kinetic model that significantly reduces complexity compared to traditional molecular fragmentation models while simultaneously improving predictive accuracy. A particularly important contribution is the first systematic treatment of the concentration divergence phenomenon observed during the transesterification reaction of BPAF and DPC. Through detailed investigation of reaction mechanisms under both catalyst-free and catalyst-assisted conditions, the study provides new understanding of the polycondensation process. Kinetic experimental fitting has yielded apparent activation energies and rate constant expressions for both catalytic regimes, enabling quantitative prediction of reaction behavior. Based on the developed model and experimental findings, the effects of temperature and catalyst concentration on chain growth during BPAF and DPC transesterification have been systematically analyzed, providing practical guidance for process optimization and scale-up. This fundamental understanding of polymerization kinetics and mechanisms is crucial for developing robust manufacturing processes capable of producing modified polycarbonates with consistent molecular weight and properties [9].

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Block copolymers combining different polymer segments offer unique opportunities for creating materials with controlled phase separation and tailored properties. A novel one-pot synthesis approach has been developed for preparing crystalline polycarbonate-polyester diblock copolymers through the copolymerization of tetrachlorophthalic anhydride, CO_2, and ethylene oxide using a metal-free catalytic system. This streamlined methodology represents a significant advancement in both synthetic efficiency and environmental sustainability by eliminating the need for metal-based catalysts. The resulting block copolymers exhibit a high melting point of up to 169 °C and two distinct glass transition temperatures, confirming the successful formation of phase-separated block structures. A key advantage of this synthetic approach is the ability to control both the length and composition of the copolymer segments, enabling systematic tuning of crystallinity and physical performance characteristics. The metal-free nature of the catalyst system is particularly attractive from both environmental and regulatory perspectives, as it eliminates concerns about metal contamination in the final products—a critical consideration for applications in biomedical devices, food packaging, and other sensitive areas. This work demonstrates that sophisticated polymer architectures can be achieved through simple, efficient, and environmentally benign synthetic methods, opening new possibilities for designing functional materials with controlled morphologies and properties [10].

The synthesis of bio-based polycarbonates from renewable resources has gained significant attention as part of the broader transition toward sustainable polymer production. A particularly promising approach involves the synthesis of poly(isosorbide carbonate) (PIC) via melt polycondensation using CO_2-based dimethyl carbonate (DMC) and bio-derived isosorbide (ISB) as reactants. A key innovation in this area is the development of a dual imidazolate ionic liquid catalyst, specifically 1-ethyl-3-methylimidazolium imidazolate ([Emim][Im]), in which imidazole functions as both the anion and cation. This unique catalyst design achieves exceptional activity, with isosorbide conversion reaching 98% and PIC molecular weight attaining 52,600 $g \cdot mol^{-1}$, significantly outperforming catalysts containing only single imidazole cation or anion components. The superior catalytic performance of [Emim][Im] can be attributed to its distinctive electronic properties: an exceptionally high cationic electrostatic potential (+53.05 kcal/mol) and a remarkably low anionic electrostatic potential (−76.12 kcal/mol). These complementary electrostatic characteristics result in the strongest relative electrophilicity and nucleophilicity within the catalytic system. Furthermore, the reduced electrostatic complementarity between cation and anion weakens ion-pair interactions, thereby enhancing the accessibility of active sites during the catalytic process. This green synthetic pathway, combining renewable bio-based monomers

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with CO_2-derived carbonate sources and an efficient ionic liquid catalyst, represents a significant step toward the sustainable production of high-performance bio-based polymers with minimal environmental impact [11].

The development of chemically recyclable polymers from renewable resources represents a critical strategy for achieving circular materials economies. Recent work on biohybrid polycarbonates derived from terpenes demonstrates the potential for creating functional materials with inherent recyclability. Through catalytic ring-opening copolymerization of 2-menthene oxide—a terpene-based monomer derived from L-menthol—with CO_2, researchers have successfully synthesized poly(menthene carbonate) with maximum molecular weights (M_n) reaching 10.2 kg mol^{-1}. The versatility of this approach is further demonstrated through formal terpolymerization processes that combine the terpene monomer with limonene oxide and CO_2, producing biohybrid polycarbonates with varying degrees of functionality depending on monomer feed ratios. The methodology can be extended to incorporate acyclic terpene oxides and previously reported xylose-derived bicyclic oxetanes, expanding the structural diversity of accessible biohybrid materials. A particularly significant feature of these biohybrid polycarbonates is their selective depolymerization capability. Under catalysis by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), the polymers can be conveniently depolymerized to regenerate the original mixture of terpene oxides with greater than 95% efficiency. This high-efficiency chemical recycling provides a practical pathway for the circular use of these biohybrid macromolecules, enabling material recovery and repolymerization without significant loss of monomer quality. The combination of renewable feedstocks, CO_2 utilization, controlled functionality, and chemical recyclability positions these terpene-based biohybrid polycarbonates as exemplary sustainable materials for future applications [12].

The efficient fixation of carbon dioxide through copolymerization with epoxides to produce polycarbonate ether polyols represents both an environmental benefit and a route to valuable degradable polymeric materials. While extensive research has focused on CO_2 copolymerization with various epoxides, studies on 1,2-butylene oxide (BO) have been relatively limited. Recent work employing layered Zn-Co double metal cyanide (L-DMC) catalysts has demonstrated exceptional performance for the copolymerization of CO_2 and BO to produce polycarbonate ether polyol. Under optimized reaction conditions, the L-DMC-mediated copolymerization exhibits remarkable activity, achieving catalytic productivity up to 1,500 g of polymer per gram of catalyst—a productivity level suitable for industrial applications. The resulting polycarbonate ether polyol incorporates a high CO_2 content, with the carbonate fraction reaching 35.5%, representing efficient CO_2 fixation. In situ FTIR spectroscopy studies have

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provided mechanistic insights, revealing a short induction period of only 10 minutes and identifying competition between polycarbonate ether polyol formation and butylene carbonate (BC) production. The L-DMC catalyst offers several practical advantages, including ease of preparation, excellent stability under reaction conditions, and outstanding catalytic performance. These characteristics, combined with the high productivity and CO_2 incorporation efficiency, suggest that L-DMC catalysts are promising candidates for large-scale production of CO_2-BO-based polymers, potentially contributing to both CO_2 utilization and the manufacture of environmentally degradable polymer materials [13].

Block copolymers with precisely controlled architectures and the ability to undergo hierarchical self-assembly are of significant interest for creating functional nanostructured materials, yet their convenient synthesis remains challenging. A novel approach involves the facile synthesis of poly(phenyl isocyanide)-block-polycarbonate copolymers using both stepwise and one-pot polymerization strategies. The key to this methodology is a specially designed hydroxyl-functionalized alkyne-Pd(II) (Pd(II)-OH) initiator, in which the Pd(II) moiety catalyzes the living polymerization of phenyl isocyanides while the terminal hydroxyl unit initiates the ring-opening polymerization of cyclic carbonates. This bifunctional initiator enables the controlled synthesis of block copolymers with desired molecular weights and narrow dispersity (Mw/Mn) distributions through both stepwise and one-pot approaches, using various phenyl isocyanides and carbonates as monomers. The synthetic versatility allows for the preparation of amphiphilic block copolymers containing hydrophilic poly(phenyl isocyanide) segments and hydrophobic crystallizable polycarbonate blocks. These amphiphilic block copolymers undergo crystallization-driven self-assembly (CDSA), forming diverse nanostructures including nanospheres, one-dimensional nanofibers, and two-dimensional nanoribbons. Importantly, the dimensions of these nanostructures—including widths and lengths—can be controlled with narrow dispersity distributions, enabling the creation of well-defined nanomaterials with predictable morphologies. This work demonstrates a practical route to complex polymer architectures and their controlled hierarchical assembly, opening possibilities for applications in drug delivery, catalysis, and functional nanomaterials [14].

The development of low-dielectric materials with excellent mechanical properties is increasingly critical for advancing high-speed communication technologies and large-scale integrated circuits. A systematic investigation of co-polycarbonates incorporating cyclohexyl and fluorene structures has demonstrated that strategic molecular design can yield materials with an optimal combination of low dielectric constant, high thermal resistance, excellent solubility, and superior

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mechanical properties. These co-polycarbonate resins, synthesized via melt transesterification, exhibit dielectric constants ranging from 2.41 to 2.71 at 1 MHz—significantly lower than conventional polycarbonates. This reduction in dielectric constant is attributed to the incorporation of non-polar fluorene groups, which decrease molecular polarization. The systematic variation of fluorene structure content enables precise tuning of material properties, demonstrating clear structure-property relationships. Beyond their electrical properties, these co-polycarbonates exhibit exceptional solubility, dissolving readily in common organic solvents including N-methyl-2-pyrrolidone (NMP), dichloromethane (CH_2Cl_2), and tetrahydrofuran (THF) at room temperature—a significant advantage for solution processing and coating applications. The materials also demonstrate impressive thermal stability, with glass transition temperatures ranging from 160.6 to 173.1 °C, and excellent mechanical properties, with tensile strengths between 50.54 and 70.72 MPa. This combination of low dielectric constant, good processability, high thermal stability, and strong mechanical performance makes these co-polycarbonates promising candidates for applications in high-frequency electronics, microelectronics packaging, and advanced circuit board materials [15].

Conclusion

The field of polycarbonate synthesis has undergone a remarkable transformation, evolving from conventional petroleum-based, phosgene-dependent processes toward sustainable, environmentally benign approaches that integrate renewable feedstocks, CO_2 utilization, and circular economy principles. The research reviewed herein demonstrates that bio-based polycarbonates derived from isosorbide, terpenes, and other renewable resources can match or exceed the performance of traditional BPA-based materials while offering superior sustainability profiles [2, 11, 12]. The successful copolymerization of CO_2 with various epoxides not only provides a route for greenhouse gas utilization but also enables access to polycarbonates with tunable properties and novel functionalities [4, 13]. These advances underscore the feasibility of decoupling high-performance polymer production from fossil resource dependence.

Catalytic innovations have been central to these achievements, with diverse systems—including metal-organic complexes, ionic liquids, double metal cyanides, and metal-free organocatalysts—demonstrating exceptional activity, selectivity, and control over polymerization outcomes [7, 10, 11, 13]. The development of bifunctional catalysts and binary catalytic systems has enabled one-pot syntheses and the creation of complex polymer architectures with precisely controlled functional groups [4, 14]. These catalytic advances, combined with sophisticated synthetic methodologies such as melt chain extension and reversible

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polycondensation, have expanded the accessible design space for polycarbonate materials [2, 6]. The ability to systematically tune molecular weight, end-group functionality, and polymer architecture provides unprecedented control over material properties, enabling optimization for specific applications ranging from low-dielectric electronics materials to flame-retardant polymers with enhanced safety profiles [8, 15].

The integration of chemical recycling and upcycling strategies represents a critical advancement toward circular materials economies. The demonstration that polycarbonates can be selectively depolymerized to recover high-purity monomers suitable for repolymerization establishes the foundation for closed-loop material lifecycles that minimize waste and resource consumption [8, 12]. Furthermore, innovative upcycling approaches that transform polycarbonate waste into Mannich polyols for polyurethane foams, or that incorporate spent lithium battery electrolytes into new polycarbonate materials, exemplify the creative strategies needed to address multiple waste streams simultaneously [3, 5]. These circular economy approaches not only reduce environmental burden but also create economic value from materials previously considered waste.

Despite these significant advances, several challenges and opportunities remain. The scalability and economic viability of bio-based polycarbonate production require continued optimization of catalytic systems, process intensification, and integration with existing industrial infrastructure. The development of more robust structure-property relationships through computational modeling and machine learning approaches could accelerate the design of application-specific materials and reduce the time from discovery to commercialization [1]. Advanced catalyst design, particularly systems that combine high activity with facile recovery and reuse, remains a priority for improving process economics and environmental footprint. Additionally, supportive policy frameworks, including incentives for renewable feedstock utilization, carbon pricing mechanisms, and extended producer responsibility schemes, will be essential for enabling the transition from laboratory innovations to industrial-scale sustainable polycarbonate production [1].

Looking forward, the convergence of sustainable chemistry, advanced materials science, and circular economy principles positions polycarbonates as exemplary materials for the transition toward carbon-neutral and resource-efficient economies. The continued development of bio-based and CO2-derived polycarbonates, coupled with innovations in chemical recycling and upcycling, offers a compelling pathway to address the interconnected challenges of plastic waste, climate change, and resource scarcity. As these technologies mature and scale, polycarbonates synthesized through sustainable routes have the potential to

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serve as models for the broader transformation of the polymer industry toward environmental responsibility and long-term sustainability. The research reviewed herein demonstrates that high-performance materials and environmental stewardship are not competing objectives but rather complementary goals achievable through thoughtful molecular design, innovative catalysis, and systems-level thinking about material lifecycles.

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