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Preparation, Depolymerization, and Recycling of Polyethylene Terephthalate in Room-Temperature Ionic Liquids

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Abstract: *The depolymerization technology of polyethylene terephthalate (PET) is crucial for degrading PET into the monomer bis (2-hydroxyethyl) terephthalate (BHET). Against the backdrop of widespread plastic usage and the inability of discarded or landfilled plastics to undergo microbial degradation, technologies enabling the conversion of waste PET into new qualified PET products for circular reuse have become particularly important and urgent. This paper systematically elaborates on the concept, physical, and chemical properties of room-temperature ionic liquids (RTILs), as well as their unique advantages as green reaction media. It further discusses PET synthesis, properties, and the recent research status, breakthroughs, and technical barriers in PET alcoholysis depolymerization using RTILs.*

Keywords: *Iionic liquid; Polyethylene terephthalate; Depolymerization; Recycling*

1. Introduction

Polyethylene terephthalate (PET), a petroleum-based polyester plastic, is widely used in bottles, packaging, textiles, and other applications due to its superior mechanical strength, electrical insulation, and fatigue resistance. However, the massive consumption of PET has adverse environmental impacts: its inherent inertness leads to extremely slow natural degradation, causing severe pollution to ecosystems and threatening human health. Statistics indicate that over 70 million tons of PET waste are generated globally annually, accounting for ~12% of total plastic waste, with less than 10% being recycled[1]. Thus, efficient degradation and recycling of PET waste to achieve plastic circularity has become a research priority.

2. Room-Temperature Ionic Liquids

Room-temperature ionic liquids (RTILs) are molten salts composed of large, symmetric or asymmetric organic cations (often with alkyl chains) and small inorganic/organic anions, held together by electrostatic interactions, and existing as liquids at or near room temperature. A defining feature of RTILs is their structural and physicochemical tunability: by modifying cations, anions, or their substituents, a diverse range of RTILs with properties from hydrophobic to hydrophilic and low to medium-high viscosity can be designed[2]. Theoretically, 10^{18} cation-anion combinations are possible, though commercially available RTILs remain far fewer. (Figure 1)

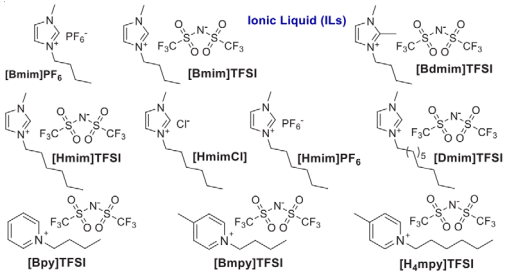

Figure 1. Common cation structures in ionic liquid systems.

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Similar to traditional molten salts, RTILs exhibit a broad liquidus range, exceeding that of most conventional solvents. Unlike high-melting molten salts (e.g., NaCl, mp 803°C), RTILs have low melting points (<100°C) due to weakened cation-anion interactions caused by large cation sizes. Their low symmetry and charge delocalization across organic cations/anions further suppress crystallization. Notably, RTILs differ from molten salt solutions (e.g., aqueous NaCl) and traditional high-temperature molten salts (corrosive viscous media like molten minerals). RTILs are typically colorless, flowable, and processable liquids at ambient conditions. Cation structure primarily determines stability, while anions influence chemical stability and functionality.

RTILs offer unique advantages: negligible volatility, non-flammability, low melting points, wide liquidus ranges, strong electrostatic fields, broad electrochemical windows, high ionic conductivity, thermal stability, selective solubility, and designability. These properties enable RTILs to replace traditional solvents, reducing environmental pollution from volatile organic compounds. In chemical reactions, RTILs provide a distinct microenvironment that enhances catalyst activity, milder conditions, faster reaction rates, and improved conversion/selectivity. Catalysts can be recycled with RTILs, combining homogeneous efficiency with heterogeneous separability-addressing the limitations of volatile, hazardous organic solvents.

3. Synthesis, Properties, and Applications of PET

Polesters, thermoplastic polymers with ester linkages in their backbone, include aliphatic (e.g. polylactic acid) and aromatic types. PET, the most important semi-aromatic polyester, features alternating ethylene glycol and terephthalic acid units linked by ester bonds (Figure 2). The benzene ring imparts rigidity, strength, and high melting points, while methylene groups provide chain flexibility, endowing PET with excellent thermal, chemical, and mechanical stability.

Commercial PET synthesis has two methods: (1) Esterification of terephthalic acid (TPA) with excess ethylene glycol (EG) at 190-250°C and 400 kPa to form BHET (Figure 3); (2) Transesterification of dimethyl terephthalate (DMT) with EG at 180°C and 100 kPa to produce BHET. BHET then undergoes prepolymerization (270°C, 2000-3300 Pa) and final polycondensation (280-285°C, 60-130 Pa) to yield high-molecular-weight PET. Industrial production relies on melt polycondensation, often followed by solid-state polycondensation to increase molecular weight.

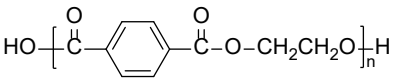

Figure 2. Main chain structure of PET macromolecules.

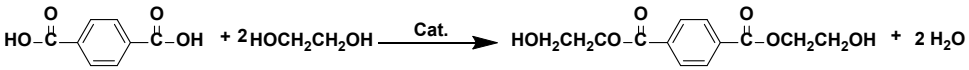

Figure 3. Reaction of terephthalic acid (PTA) with ethylene glycol (EG) to form bis (2-hydroxyethyl) terephthalate (BHET).

Melt polycondensation typically requires high temperatures (>250°C), high vacuum, and long reaction times, raising environmental concerns. Liu et al.[3,4] developed a two-step polycondensation using benzylimidazolium and phenylalkylpyrrolidinium RTILs for BHET post-polycondensation, achieving high-molecular-weight PET under milder conditions (Figure 4)[4]. The process involves: (1) Prepolymerization: DMT and EG undergo transesterification with Mn/Mg catalysts to form low-degree (2-4) BHET oligomers; (2) Post-polycondensation with Sb catalysts under heating/vacuum to produce high-molecular-weight PET. Methanol and EG are byproducts of transesterification and polycondensation, respectively.

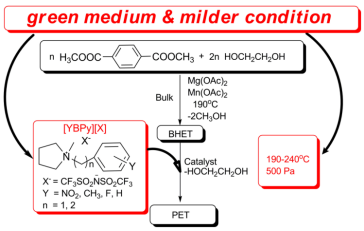

Figure 4. Two-step polycondensation for high-molecular-weight PET in phenylalkylpyrrolidinium ionic liquids.

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Efficient removal of small-molecule diols is critical for high-molecular-weight PET. RTILs' low volatility allows their use as reaction media under high vacuum, diluting viscous polymer solutions and facilitating byproduct removal. PET properties (molecular weight, intrinsic viscosity [IV]) are tailored for applications: fiber-grade PET (IV 0.55-0.67 dL g^{-1}, M_n 15,000-20,000 g mol^{-1}) contains TiO_2 as a matting agent; bottle-grade PET (IV 0.75-1.00 dL g^{-1}, M_n 24,000-36,000 g mol^{-1}) requires transparency and food safety compliance; industrial tire cords demand ultra-high IV (>0.95 dL g^{-1}, M_n 40,000-50,000 g mol^{-1}).

PET's semi-crystalline nature (30-40% crystallinity) enables applications in films, containers, and fibers. However, most PET products are single-use, leading to accumulation of non-biodegradable waste.

4. Recycling Methods for PET Waste

Waste plastics represent a cost-effective feedstock for producing new chemicals and energy. PET recycling methods include:

● Mechanical recycling: Converts waste into pellets/flakes without altering chemical structure, but performance degrades with repeated cycles.

● Energy recovery: Incineration generates ~46,000 kJ kg^{-1} (vs. 20,000 kJ kg^{-1} for coal), but releases toxic emissions (e.g., dioxins) and wastes resources.

● Chemical recycling: Depolymerizes PET into monomers/oligomers via chemical reactions (hydrolysis, glycolysis, acidolysis, etc.)[5,6], enabling re-polymerization into high-value products (Figure 5)[7].

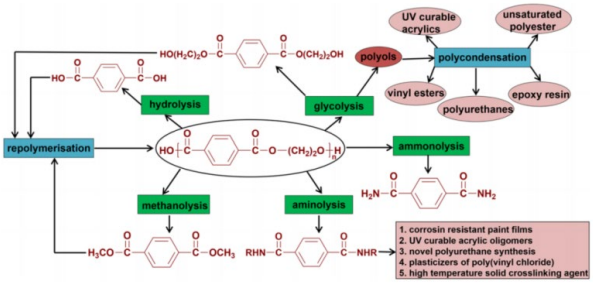

Figure 5. Different chemical depolymerization methods for PET and value-added products.

Hydrolysis cleaves PET into TPA and EG under neutral, acidic, or alkaline conditions. Neutral hydrolysis avoids corrosive reagents but requires high temperature (200-300°C), pressure (15 atm), and long reaction times (6-24 h). Acid/alkaline hydrolysis generates toxic byproducts or salts, limiting scalability.

Glycolysis, the most widely adopted chemical method, uses alcohols (e.g., EG) as solvents/reactants under mild conditions (<190°C, atmospheric pressure) to produce BHET. Advantages include low volatility/corrosivity, no wastewater, and suitability for continuous production. Catalysts (e.g., metal salts, RTILs) are critical to accelerate reactions. Metal catalysts (e.g., Sb_2O_3, $Zn(OAc)_2$) achieve high efficiency but suffer from cost and metal residue issues[8–11]. Microwave irradiation enhances rates: Enayati et al.[11] reported 96.7% PET conversion with Sb_2O_3 (0.25 wt%) at 240°C for 5 minutes.

5. PET Depolymerization in Ionic Liquids

RTILs' designability and green credentials make them ideal solvents/catalysts for PET depolymerization. PET solubility, a key factor, depends on RTIL structure: cations like $[BMIM]^+$ paired with anions (Cl^-, Br^-, CF_3COO^-, CH_3COO^-, $AlCl_4^-$) promote dissolution via hydrogen bonding with carbonyl oxygens and C-O bond cleavage[12].

For example, using 1-butyl-3-methylimidazolium chloride as solvent and acid-functionalized 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate as catalyst, PET hydrolysis at 170°C for 4.5 h achieved 100% conversion and 88% TPA yield, with RTIL recyclability over 8 cycles[13]. Yang et al.[14] demonstrated TPA as a recyclable catalyst, achieving 95.5% TPA purity at 220°C for 3 h. Lu et al.[15] synthesized 1-ethyl-3-methylimidazolium terephthalate, avoiding metal impurities and reducing rPET

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discoloration via hydrogen bonding between TPA carboxyl groups and EG hydroxyls.

Cholinium-based RTILs, developed by Zhang's group[15], offer biocompatibility and low cost. At 180°C and atmospheric pressure with EG, acetylcholine catalyst achieved 85.2% BHET yield in 4 h. Amino acid-based RTILs further improved efficiency: complete PET degradation in 125 minutes at 93.5°C with 88.7% BHET yield[16,17]. However, cholinium cations were not critical to catalysis[18]. (Figure 6)

Bharti et al.[19] evaluated 121 RTILs for glycolysis, highlighting challenges in structure-activity relationship analysis due to variable feedstocks and reaction conditions. Connon et al.[20] optimized 33 RTILs, identifying biodegradable catalysts with superior activity to cholinium glycinate (Figure 7).

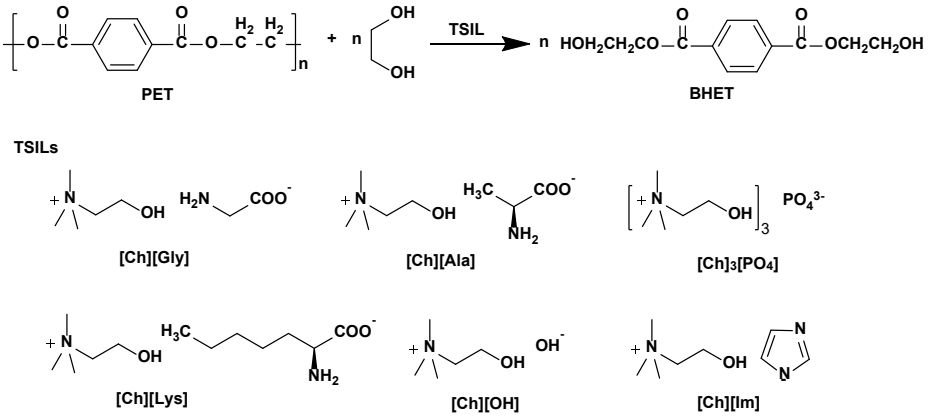

Figure 6. PET glycolysis reaction and structures of selected choline-amino acid ionic liquids.

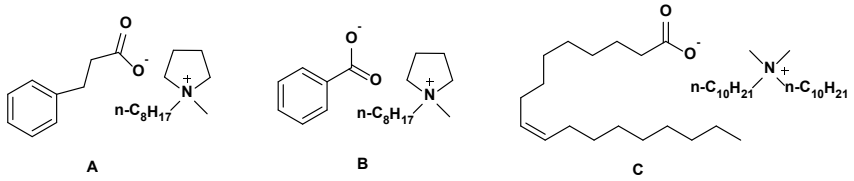

Figure 7. Ionic liquid catalysts with PET glycolysis activity and biodegradability.

6. Circular Economy of PET Recycling

PET life-cycle management is pivotal for circular economy transitions. Recycling reduces landfill pollution and energy consumption by 50-60% compared to virgin production. "Bottle-to-bottle" closed-loop systems enable waste PET to re-enter production as fibers or raw materials.

Challenges include inadequate collection networks, low public awareness, low-value mechanical recycling, immature chemical technologies, and insufficient policy support. Addressing these requires improved infrastructure, R&D investment, regulatory incentives, and public education.

7. Conclusion

PET's ubiquity in packaging, textiles, and manufacturing drives urgent demand for sustainable management. Transitioning from linear to circular economies necessitates interdisciplinary innovations in polymer science and green chemistry. RTIL-based depolymerization technologies offer promising solutions for efficient, low-impact PET recycling, supporting global plastic pollution mitigation and resource conservation.

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