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Viewpoint

# Ionic-Liquid-Mediated Deconstruction of Polymers for Advanced Recycling and Upcycling

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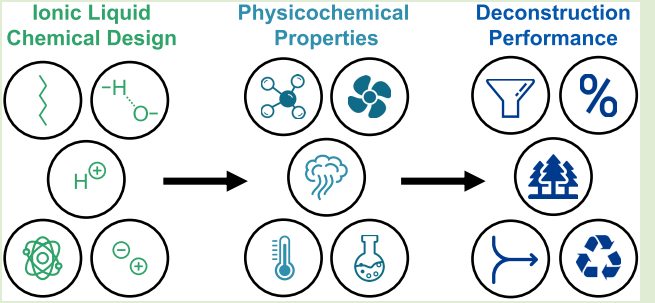
**ABSTRACT:** Ionic liquids (ILs) are a promising medium to assist in the advanced (chemical and biological) recycling of polymers, owing to their tunable catalytic activity, tailorable chemical functionality, low vapor pressures, and thermal stability. These unique physicochemical properties, combined with ILs' capacity to solubilize plastics waste and biopolymers, offer routes to deconstruct polymers at reduced temperatures (and lower energy inputs) versus conventional bulk and solvent-based methods, while also minimizing unwanted side reactions. In this Viewpoint, we discuss the use of ILs as catalysts and mediators in advanced recycling, with an emphasis on chemical recycling, by examining the interplay between IL chemistry and deconstruction thermodynamics, deconstruction kinetics, IL recovery, and product recovery. We also consider several potential environmental benefits and concerns associated with employing ILs for advanced recycling over bulk- or solvent-mediated deconstruction techniques, such as reduced chemical escape by volatilization, decreased energy demands, toxicity, and environmental persistence. By analyzing IL-mediated polymer deconstruction across a breadth of macromolecular systems, we identify recent innovations, current challenges, and future opportunities in IL application toward circular polymer economies.






Plastics are ubiquitous in modern society owing to their low cost and widely tunable properties that can be leveraged across many industries. Since reaching commercial viability in the 1950s, plastics production has grown faster than that of other manufactured materials.[1] The widespread use of plastics has improved quality of life and replaced alternative materials due to generally lower energetic and environmental costs in primary production;[2,3] however, the lack of appropriate infrastructural and societal systems for plastics waste management has become a significant burden.[4,5] To date, most plastics waste has been directed to landfills, incinerated, or leaked into the environment,[1] where it can persist for years as microplastics and in other forms.[6,7] This problem, combined with a reliance on fossil fuel resources for monomer feedstocks,[8] energy costs associated with plastics synthesis and processing,[9] and public awareness,[10,11] has invigorated interest and research in methods to capture and repurpose plastics waste.

The most prevalent strategy for reconditioning end-of-life plastics is mechanical recycling.[12,13] In mechanical recycling, mixed plastics waste streams are typically separated by chemical identity, and the resultant homogeneous plastics streams are ground, melted, pelletized, and reused for new applications.[2,13] Generating plastics materials from mechanical recycling outputs can offset demand for virgin petrochemical feedstocks and lower environmental burdens from plastics waste;[4] however, mechanical recycling alters the underlying macromolecules (e.g., through chain scission and cross-linking, as well as inducing color changes), severely limiting the potential number of cycles for the polymers' reuse and downgrading the potential applications of the recycled materials.[13−16] Additionally, the cost and effort associated with separating plastics waste to produce high purity streams for mechanical recycling constrains the process to plastics with limited additives in configurations that are easily separable from mixed waste streams.[17] As a consequence, only certain types of plastics, primarily polyethylenes and poly(ethylene terephthalate) (PET), are widely recycled.[18]

In recent years, increased attention has been devoted to advanced recycling processes as an alternative or complement to mechanical recycling.[19,20] More specifically, polymers subjected to advanced recycling can be depolymerized to their constituent monomers that can be used to regenerate the original macromolecules or deconstructed into other small molecules or oligomers that serve as feedstocks for synthesiz-

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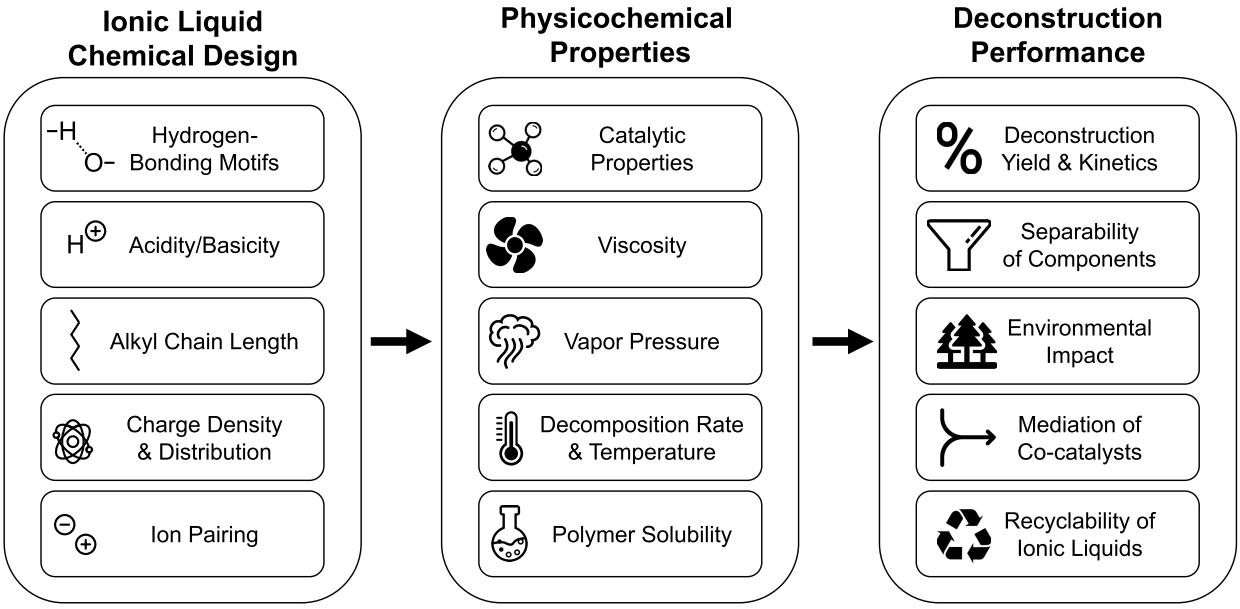
**Scheme 1. Chemical Design of ILs Can Be Harnessed to Impart Desired Physicochemical Properties and, in Turn, Impact Deconstruction Performance**




ing new materials.[16,21−23] Herein, we focus primarily on chemical recycling, which may offer a strategy to "close the loop" on the plastics life cycle if (1) chemical recycling can efficiently achieve high yields of valuable chemicals, feedstocks, and building blocks; and (2) societal and infrastructural changes enable the capture of plastics more effectively at their end-of-life.[24,25]

The principles that underpin the chemical recycling of plastics similarly have found use in the deconstruction and valorization of biopolymers to create sustainable small-molecule feedstocks.[26−28] Biopolymer deconstruction offers a pathway to using renewable, carbon-neutral materials in place of petroleum-derived compounds.[28,29] In some cases, the waste streams from biomass-intensive industrial processes (e.g., lignin from pulping operations) may serve as the inputs for polymer deconstruction to produce commercially useful small molecules, lessening the environmental impact of existing manufacturing by reducing waste.[30] Products resulting from biopolymer deconstruction, including phenolics and sugar alcohols, are useful as, e.g., biofuels, commodity chemicals, pharmaceuticals, and monomers for sustainable plastics.[30−33]

Chemical recycling may be performed in bulk with neat polymers or in solvent. Neat deconstruction (e.g., bulk thermal depolymerization, pyrolysis) often requires high temperatures and significant energy input (e.g., from pulling a high vacuum) and can be prone to the formation of unwanted byproducts, owing to the harsh conditions.[34−36] Pyrolysis deconstruction kinetics are further hampered by heat and mass transfer effects that progressively slow the deconstruction rate as the polymer dimensionality (e.g., thickness) increases.[37,38] Neat polymer deconstruction may be aided by catalysts to enable new chemical routes for producing small molecules or to reduce heat or pressures needed in bulk recycling strategies.[16,39] However, the catalysts used in these processes may be expensive, are impeded by common polymer additives, and can be difficult to separate from deconstruction byproducts for regeneration.[16,39]

In contrast, solvent-mediated chemical recycling can enable deconstruction pathways with reduced energy demands versus bulk processes and more efficient mixing between catalysts and substrates to enhance deconstruction outcomes (e.g., kinetics and selectivity).[40−43] Unfortunately, many solvent-based processes are hindered by limited solubility for combinations of catalysts and polymers or multipolymer waste streams.[44] Solvent selection also is constrained by solvent boiling points relative to the temperature at which deconstruction effectively proceeds,[45−47] significantly limiting the library of potential solvents for a given materials stream. For cases in which a solvent-mediated route for a deconstruction is identified, solvent escape, flammability, and costs associated with solvent recovery and recycling can further limit implementation.[48−50]

Ionic liquids (ILs), conventionally defined as compounds composed entirely of ions with melting points below 100 °C,[51] have unique physicochemical properties that could address some of the abovementioned hurdles to solvent-based chemical recycling. ILs are generally more thermally stable (e.g., higher boiling and decomposition temperatures) than molecular solvents and can effectively solubilize a broad range of polymer and nonpolymer species.[52,53] Notably, the chemical design of ILs also can be harnessed to impart catalytic properties for chemical transformations,[54−57] a promising feature to facilitate polymer deconstructions. Herein, we discuss the current understanding of the chemical design-property-performance relationships of ILs for polymer deconstruction to uncover opportunities and challenges in the application of ILs for chemical recycling (Scheme 1).

## IL DESIGN DETERMINES PHYSICOCHEMICAL PROPERTIES

ILs can fulfill one or several roles in a deconstruction reaction, including as a solvent, catalyst or cocatalyst, or reactant. Consequently, they can partially or entirely replace the nonpolymeric components of a deconstruction milieu. In this section, we discuss the physicochemical properties of ILs that are important to polymer deconstruction. As a note to the reader, ILs are often referred to by acronyms due to their long chemical names arising from their complex chemical nature. In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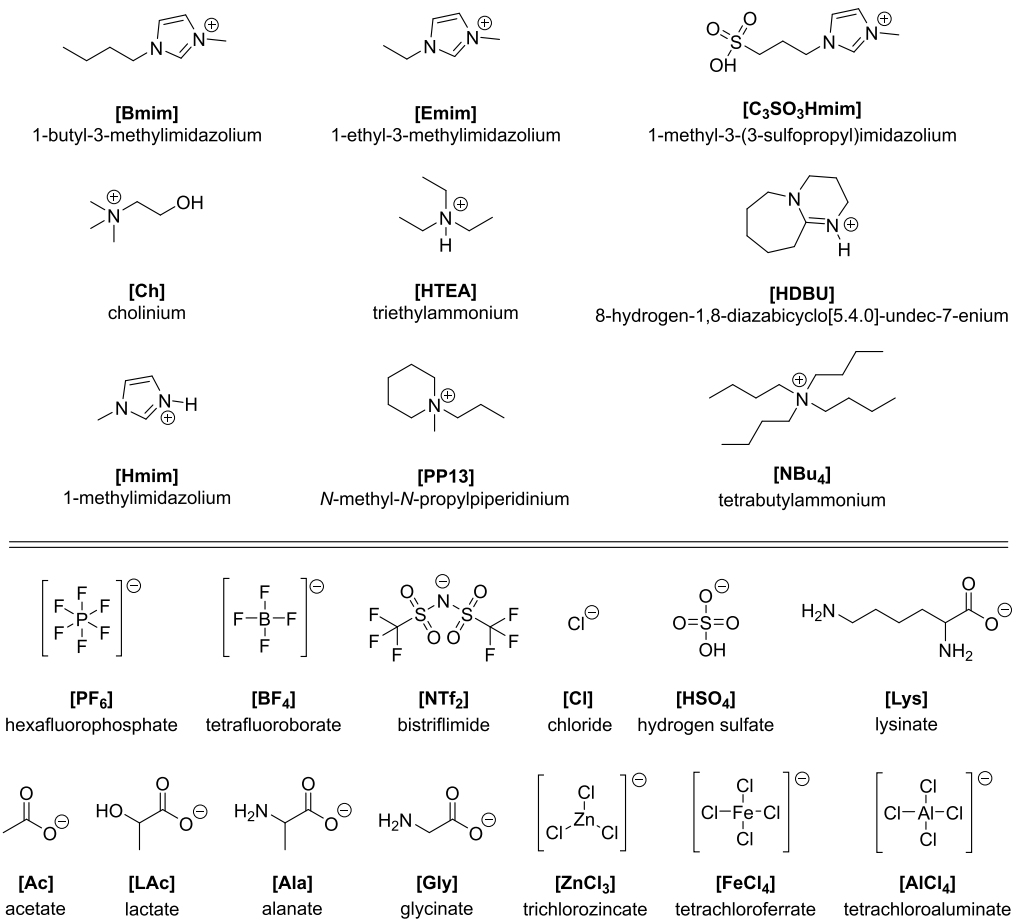


**Figure 1.** Chemical identity and combination of constituent ions determine the physicochemical properties of an IL. Cation (above) and anion (below) chemical structures of ILs discussed in this Viewpoint and the corresponding abbreviations are compiled here and showcase the breadth of chemistries used in IL design.

this Viewpoint, we adopt the common naming convention "[cation abbreviation][anion abbreviation]" and summarize major chemical names and structures in Figure 1. We direct readers to this figure and the abbreviations list at the end of the manuscript for full chemical names rather than defining each IL as it is introduced in the manuscript.

This Viewpoint considers IL systems spanning a wide range of IL subclassifications, including (but not limited to) aprotic ILs, protic ILs, acidic ILs, basic ILs, and task-specific ILs. Aprotic ILs are comprised of cations and anions that combine to form liquids without proton dissociation; in contrast, counterions in protic ILs transfer protons between Brønsted acids and bases.[58] Acidic and basic ILs take on acidic and basic characteristics, respectively, governed by the chemical functionalities that may be present on the cation, anion, or both.[59] Task-specific ILs harness chemical design to incorporate functional groups into IL chemistries that impart reactivity or physicochemical properties desirable for targeted applications.[60] ILs often belong to several of these subclassifications because of overlaps between these categories (e.g., a protic IL optimized for polymer deconstructions with acidic characteristics).[59] More recently, deep eutectic solvents, combinations of compounds that liquefy due to hydrogen-bonding (rather than ionic) interactions, have risen in interest as potential alternatives to ILs.[61] Additionally, ionic systems that liquefy below deconstruction operating temperatures, but above 100 °C, have been investigated as catalysts for deconstruction.[62−64] Such systems are outside the scope of this Viewpoint because they do not meet the classical definition of ILs, but we direct readers to the available literature for more information.[62−64]

ILs are renowned for their broad solubilities of organic and inorganic species, which can provide versatility to deconstruction reactions.[65,66] Solubility parameters like the Hildebrand and Hansen parameters are widely used to predict the solubility of polymers (and other organic species) in molecular solvents based on a "like dissolves like" description.[67] However, such parameters are broadly unreliable in describing the solubility of polymers in ILs.[53,68] For example, the solubility of poly(methyl methacrylate) varies widely among ILs with near-identical Hildebrand solubility parameters.[69] As a result, researchers have turned their attention toward multiparameter solubility models to describe polymer solubility in ILs. Of note, the hydrogen-bonding behavior of ILs has emerged as a dominant characteristic in quantifying the capacity of ILs to dissolve polymers.[70] The Kamlet−Abraham−Taft scale, which combines parameters for polarity, hydrogen-bond-donating character, and hydrogen-bond-accepting character, has found increasing prominence in the prediction of IL solvation properties.[70−73] This scale can explain qualitative observations that acidic and basic ILs readily dissolve basic and acidic polymers, respectively, when IL polarities are broadly similar.[70,74] Computational screening of IL−polymer interactions has further supported that hydrogen-bond interaction energies have the strongest influence on


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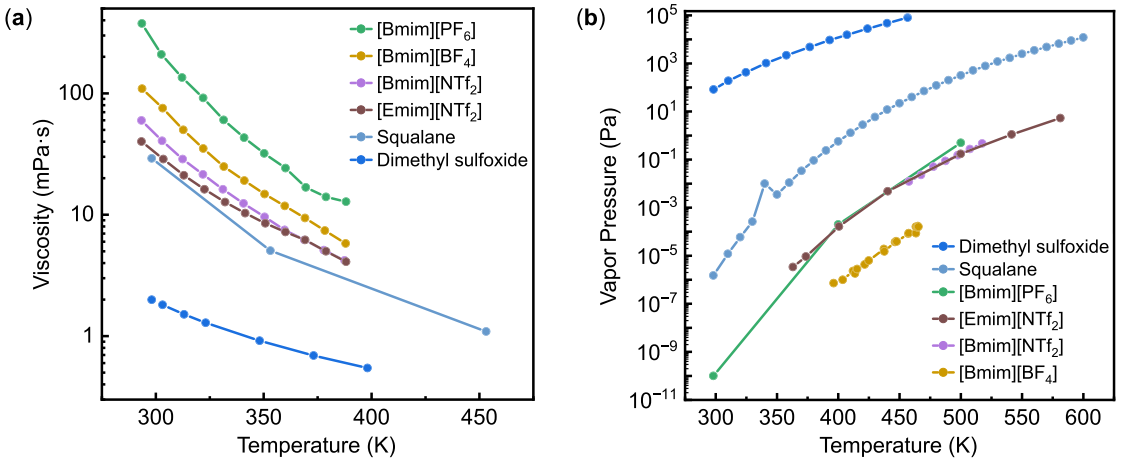


**Figure 2.** Physicochemical properties of ILs are sensitive to temperature. (a) ILs approach room-temperature viscosities of molecular solvents like squalane at temperatures within 100 K of room temperature.[84−86] (b) The vapor pressures of ILs are orders of magnitude below those of molecular solvents across experimental temperature ranges.[86,96−100]

polymer dissolution in ILs, followed by electrostatic and van der Waals forces.[75] Interactions arising from the IL anions and cations were found to have similar impacts on polymer solubilities.[75]

Viscosity is also an important consideration in IL systems. ILs' ambient- or near-ambient-temperature viscosities typically range from 10 to 500 mPa·s, one to two orders of magnitude higher than common molecular solvents, creating challenges with IL handling at room temperature.[76] The high viscosity of ILs is largely attributable to a combination of hydrogen-bonding, electrostatic, and van der Waals interactions.[76−78] Consequently, there is significant potential to use the chemical design of ILs to control viscosity.[79] For example, increasing the carbon chain length in alkyl IL cations results in a predictable increase in the room-temperature viscosity of imidazolium-based ILs.[80] Anion selection also can influence room-temperature viscosity over an order of magnitude.[80] The presence of impurities further strongly impacts the viscosity of ILs. Notably, water loadings as low as 1.5 wt % can reduce IL viscosities over an order of magnitude,[81] and the chemical identity of ILs can be chosen to control IL equilibrium and saturated water contents.[82] Thus, the presence of water and other impurities in ILs should be thoroughly characterized and may be exploited to control viscosities for deconstruction reactions.

The viscosities of ILs also demonstrate a notable sensitivity to temperature, with easier handling (e.g., significantly lower viscosities) at elevated temperatures (Figure 2a).[83,84] For example, the viscosity of [Bmim][$PF_6$] drops from ∼376 (at 20 °C) to ∼24 mPa·s (at 87 °C),[84] the latter of which is below the room-temperature (20 °C) 29 mPa·s viscosity of squalane.[85] Although current understanding supports the observation that the high-temperature viscosities of ILs fall below room-temperature viscosities of common molecular solvents,[83,84] there exists limited literature that quantitatively examines the high-temperature (>100 °C) viscosities of ILs. Given the importance of viscosity in deconstruction reactions, the experimental characterization of IL viscosities at deconstruction temperatures is worthy of further investigation to enable direct comparison to molecular solvents.[85,86]

ILs are widely known for their thermal stability that arises from intermolecular cohesion,[87] enabling the use of ILs in high-temperature deconstructions, such as the depolymerization of Nylon-6 at 300 °C.[88] However, IL decomposition temperatures are most often obtained through thermogravimetric analysis (TGA), a technique that is impacted by a variety of experimental parameters (e.g., heating rate, gas choice and flow rate, sample purity) and may not be representative of deconstruction conditions.[89,90] As one example, the reported TGA-based decomposition temperature of [Emim][$NTf_2$] varies significantly from 410−455 °C,[89] and isothermal experiments on the same IL indicate 1% mass loss within 1 h below 300 °C and within 10 h below 250 °C.[91] Though these degradation temperatures surpass the boiling points of most organic solvents to enable high-temperature deconstructions,[92] researchers are nonetheless encouraged to quantify IL decomposition or vaporization under representative reaction conditions to ensure IL loss is fully considered in a deconstruction system.

ILs are commonly acknowledged for having "negligible vapor pressures",[93−95] and although this notion is not strictly accurate, ILs' extraordinarily low vapor pressures relative to molecular solvents make them attractive for deconstruction setups by potentially enabling process intensification (e.g., simultaneous depolymerization and monomer distillation; Figure 2b).[86,96−100] As one point of reference, the vapor pressure of dimethyl sulfoxide ranges from approximately $10^{1.9}$ to $10^{4.9}$ Pa from 25 to 180 °C,[86] while the vapor pressure of [Bmim][$PF_6$] ranges from approximately $10^{-10}$ to $10^{-0.3}$ Pa from 25 to 225 °C.[97] It should be noted that there is significant experimental difficulty in obtaining reliable vapor pressure measurements for ILs, and consequently, there is broad dispersity in reported values for a given IL system.[101] Nevertheless, these low vapor pressures reduce the risk of losing solvent to evaporation during deconstruction, minimize the release of volatile organic compounds (VOCs), and offer lower flammability than many molecular solvents.[102−104] Limited IL volatility can be harnessed to evaporate the resultant small molecules from a reaction mixture and drive the equilibrium toward deconstruction, offering facile separation of products from the starting material and the chosen IL (discussed in more detail later).[105]


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Table 1. Comparison of IL-Mediated Polymer Deconstruction Performance to Other Systems[a]

| polymer [desired small molecule from deconstruction] | IL system | comparative deconstructions | |
|---|---|---|---|
| **poly(ethylene terephthalate)** | **[Bmim][$ZnCl_3$]**[118] | **catalytic glycolysis**[119] | **acidic hydrolysis**[120] |
| [bis(hydroxyethyl) terephthalate] | conversion: 98% | conversion: quantitative | conversion: quantitative |
| [I][dimethyl terephthalate] | yield: 83% | yield: 60% | yield: quantitative[I] |
| | 5 h, 180 °C | 1 h, 185 °C, organocatalyst | 5 h, 150 °C, 10 M $H_2SO_4$ |
| **poly(3-hydroxybutyrate)** | **[Emim][Ac]**[106] | **pyrolysis**[121] | **basic hydrolysis**[122] |
| [crotonic acid] | conversion: quantitative | conversion: 99% | conversion: 74% |
| | yield: 97% | yield: 84% | yield: 25% |
| | 1.5 h, 140 °C | 0.5 h, 290 °C, 150 mbar | 4 h, 190 °C, 4 M NaOH |
| **poly(bisphenol A carbonate)** | **[HDBU][LAc]**[107] | **pyrolysis**[108] | **basic alcoholysis**[123] |
| [bisphenol A] | conversion: quantitative | conversion: 70% | conversion: quantitative |
| | yield: 99% | yield: 10% | yield: 95% |
| | 1 h, 120 °C | 0.28 h, 550 °C, $N_2$ atmosphere | 0.58 h, 40 °C, catalytic NaOH, tetrahydrofuran |
| **chitin** | **[$C_3SO_3$Hmim][$HSO_4$]**[111] | **acidic hydrolysis**[124] | **biphasic acidic hydrolysis**[125] |
| [levulinic acid] | conversion: not reported | conversion: not reported | conversion: 74% |
| | yield: 67% | yield: 38 wt % | yield: 29% |
| | 5 h, 180 °C, deionized water | 0.5 h, 190 °C, microwave | 1 h, 150 °C |
| **poly(lactic acid)** | **[Bmim][$HSO_4$]**[126] | **catalytic methanolysis**[127] | **solvothermal ethanolysis**[128] |
| [methyl lactate] | conversion: 97% | conversion: quantitative | conversion: quantitative |
| [II][ethyl lactate] | yield: 93% | yield: 100% | yield: 99%[II] |
| | 3 h, 115 °C, methanol | 8 h, 80 °C, Ar flow | 1 h, 260 °C, $N_2$ atmosphere |
| **Nylon-6** | **[PP13][$NTf_2$] + DMAP**[129] | **acidic hydrolysis**[130] | **hydrothermal**[131] |
| [caprolactam] | conversion: not reported | conversion: not reported | conversion: quantitative |
| [III][aminocaproic acid] | yield: 86% | yield: 94%[III] | yield: 85% |
| | 1 h, 300 °C, $N_2$ atmosphere | 8 h, 40 vol % HCl | 1 h, 300 °C, subcritical $H_2O$, Ar atmosphere |
| **polyethylene** | **[Emim][$AlCl_4$]**[132] | **catalytic hydrogenolysis**[133] | **pyrolysis**[134] |
| [liquid and gaseous alkanes] | conversion: not reported | conversion: quantitative | conversion: 97% |
| [IV][liquid and gaseous hydrocarbons] | yield: 95 wt % | yield: quantitative | yield: 97 wt %[IV] |
| | 72 h, 120 °C, mixed with acidic cocatalyst | 12 h, 280 °C, 30 bar $H_2$ atmosphere | 0.75 h, 450−470 °C, $N_2$ flow |

[a]Conversion describes the loss in mass of the starting polymer as a result of undergoing deconstruction, and yield describes the amount of captured small-molecule products relative to the theoretical maximum of product. Conversions and yields selected for this table are from the most optimized conditions in each report and provided on a mass and molar basis, respectively, unless otherwise noted. The conditions included in each cell are intended to give context for, rather than exhaustively describe, the deconstruction parameters and environment.

## IL PHYSICOCHEMICAL PROPERTIES IMPACT DECONSTRUCTION PERFORMANCE

The catalytic properties of ILs can be tailored through chemical design to enable efficient polymer deconstructions, often producing small-molecule products at higher yields and lower energy demands than those of prototypical strategies (Table 1). An increasing body of literature indicates that the acidic or basic nature of ILs dictates IL-mediated deconstruction performance, in contrast to deconstruction in molecular solvents in which monomer solubility has a dominant role.[45] For example, the base-catalyzed deconstruction of poly(3-hydroxybutyrate) (PHB) proceeds rapidly to high yield in the presence of the basic [Emim][Ac] IL (97 mol % yield, 90 min, 140 °C), but does not occur with the less basic [Emim][Cl] IL (Figure 3a).[106] A similar trend is revealed in the alcoholysis of polycarbonate (PC) in which highly basic [HDBU]-based ILs produce near quantitative yields of bisphenol A (BPA), whereas neutral or acidic ILs yield less BPA (0−90 mol %).[107] The optimized IL-mediated PC deconstruction provides significant advantages in yield and reaction conditions over PC pyrolysis. For instance, pyrolysis is prone to significant byproduct formation that in turn demands extensive separations to obtain BPA but with lower yields (10 mol % yield, 550 °C, 17 min, $N_2$ atmosphere).[108]

Acidic ILs have likewise demonstrated efficient use in acid-catalyzed deconstructions, as in the depolymerization of PET.[109] Currently, only limited examples are available that compare the acid-catalyzed deconstruction performance of ILs with differing acidities for plastics systems. However, investigations of biopolymer deconstructions with systematic changes in IL chemistry find that increasing IL acidity enhances acid-catalyzed deconstruction performance.[110,111] For example, the ether cleavage rate during lignin deconstruction increases as the acidity of the IL increases.[110] Similarly,


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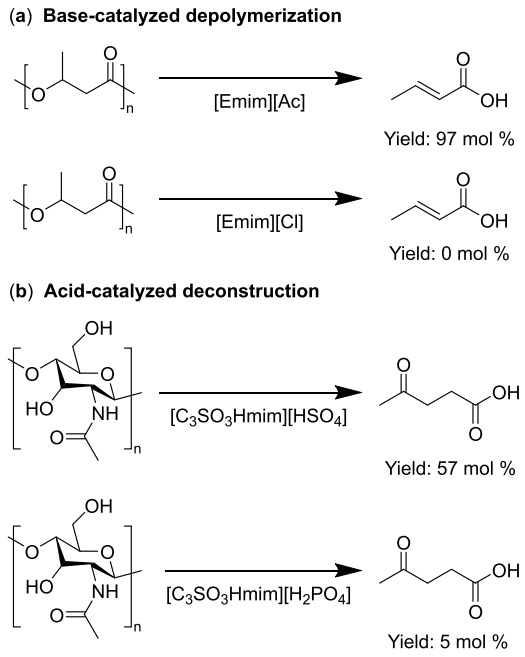


**Figure 3.** Small-molecule yields are well correlated with the acidity or basicity of the ILs used in polymer deconstructions. Here, selected examples show the influence of counterion acidity or basicity in (a) the base-catalyzed deconstruction of poly(3-hydroxybutyrate)[106] and (b) the acid-catalyzed deconstruction of chitin.[111]

the yield of levulinic acid from the acid-catalyzed deconstruction of chitin is well-correlated to the Brønsted acidities of the IL medium (Figure 3b).[111] These results underscore the impact of incorporating acidic or basic characteristics into IL design for catalyzing the corresponding deconstruction mechanism.

The effect of IL acidity or basicity on deconstruction performance can be complicated by steric effects in IL design. In the base-catalyzed deconstruction of PET by amino acid–based ILs, the least sterically hindered glycine-containing [Ch][Gly] IL demonstrated notably higher small-molecule yields (43 mol % yield) vs lysine-containing [Ch][Lys] (24 mol % yield) or alanine-containing [Ch][Ala] (0 mol % yield) ILs with similar anion acid dissociation constants under the same conditions (6 h, 150 °C).[112] Similarly, in the aforementioned alcoholysis of PC, equivalently acidic ILs with differing steric hindrances showed markedly different catalytic activities. For example, the sterically hindered [HTEA][LAc] yielded just 10 mol % BPA, while the less bulky [Hmim][LAc] yielded 90 mol % BPA under identical reaction conditions.[107]

The ability to disrupt inter- and intramolecular hydrogen bonding in polymeric systems offers another vital parameter in IL design to enhance deconstruction. Hydrogen bonding between ILs and PET influences, among other parameters, backbone PET bond lengths and angles, charge densities, and electronegativities, synergistically promoting PET deconstruction.[113] For example, [Ch][Ac] with a calculated 453 kJ/mol binding strength to PET model dimers deconstructed PET at a 94 wt % conversion to a small-molecule product in 83 mol % yield.[113] In contrast, [Ch][Cl] at a comparatively weaker 424 kJ/mol binding strength deconstructed PET with a 3 wt % conversion to no capturable small-molecule product.[113] This effect is particularly important for polymers with properties that are dominated by hydrogen-bonding effects (e.g., polyamides).[114]

Metallic atoms also can be added into the design of ILs, often in the form of metal salts, to promote deconstruction. These metals can coordinate with hydrogen-bonding groups in condensation polymers to cause rapid deconstructions with high yields.[115−117] For example, [Bmim][$ZnCl_3$] ILs have been used as the deconstruction medium for PET with an 83 mol % yield of bis(hydroxyethyl) terephthalate (5 h, 180 °C).[118] This performance falls between typical outcomes for PET deconstruction by catalytic glycolysis[119] and acidic hydrolysis,[120] but it avoids the potentially complicated removal of catalysts or the use of concentrated acids (e.g., 10 M sulfuric acid) needed to achieve high yields. Similarly, synergistic effects between the cation and anion of a [Bmim][$FeCl_4$] IL result in higher deconstruction catalytic activities at lower temperatures for PET versus either the analogous metal-free [Bmim][Cl] IL or the $FeCl_3$ salt alone.[135] The incorporation of metallic atoms into ILs also has shown promise for polyolefin deconstruction.[136] For instance, a Lewis acid chloroaluminate-based IL facilitated the upcycling of polyethylene to liquid alkanes by enabling simultaneous cracking and alkylation. This system achieved quantitative polyethylene conversion to isoalkanes within 6 h at 70 °C, and the small-molecule outputs phase-separated from the IL reaction milieu to enable facile recovery of the product.[136]

It is worth noting that several experimental parameters interact with IL design to determine the effectiveness of IL-mediated deconstruction. For example, temperature plays a controlling role in overcoming the activation energy to enable catalytic reactions.[88,137] The concentration of the polymer species also has a critical role in its IL-mediated deconstruction. In general, increasing polymer concentrations in ILs increases the polymer degradation rate, as in the deconstruction of PET.[138] However, high polymer concentrations (e.g., >40 wt % polymer in IL) can impede deconstruction when hydrogen bonding is possible between the IL and the polymer, as demonstrated in the deconstruction of PHB.[106] The presence of impurities, especially water, also can influence deconstruction thermodynamics.[106,139] In PET glycolysis, water loadings as low as 4 wt % can halve reaction conversion (1 atm, 180 °C, 8 h) due to the coordination of water protons with the IL anions.[139] The same effect transpires at higher water loadings (25−50 wt %) in the deconstruction of PHB but is less influential at lower water loadings (2.5 wt %).[106]

In short, the chemical design of ILs can be exploited to enhance catalytic deconstruction through control of IL acidity/basicity, sterics, hydrogen bonding, and reactive sites. These characteristics can be tuned through changes to experimental parameters, namely, temperature, polymer concentration, and impurities. Researchers are thus offered a wide experimental design space when ILs are used for deconstruction.

## ■ ILS SOLUBILIZE AND SYNERGIZE NON-IL CATALYSTS

The previous section discussed how ILs can be used in isolation as simultaneous deconstruction catalysts and solubilizing agents. Here, we describe how ILs find additional utility in enhancing the performance of non-IL catalysts in the deconstruction of plastics and biopolymers.

At the simplest level, ILs may be used as high-temperature-stable, polymer-dissolving solvents for deconstructions involving non-IL catalysts. Among organic catalysts, 4-dimethylami-


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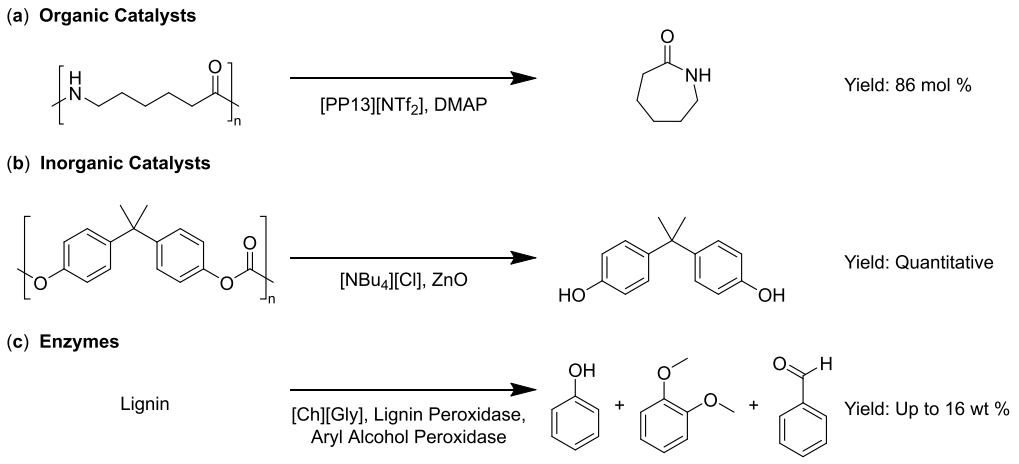


**Figure 4.** ILs may be combined with other catalysts to mediate deconstruction reactions. (a) Organic catalysts like DMAP are used effectively in ILs to depolymerize polyesters and polyamides like Nylon-6.[129] (b) ILs can enhance the catalytic properties of inorganic catalysts, such as zinc oxide in the deconstruction of PC.[144] (c) Typically recalcitrant biopolymers like lignin can be dissolved in ILs for enzyme-mediated deconstructions that are challenging in molecular solvents.[151]

nopyridine (DMAP) has found significant use as a deconstruction catalyst. Low loadings (<10 wt % relative to monomer) of DMAP are recognized to catalyze transesterification and alcoholysis reactions, leading to its use in the deconstruction of PC, poly(lactic acid), and PET.[140−142] Specific combinations of ILs and DMAP were found to enhance the yield of caprolactam from Nylon-6 depolymerization at 300 °C over ILs alone, indicating a synergistic effect may be present when ILs and DMAP are used in tandem for deconstructions.[129,143] Though [PP13][$NTf_2$] catalyzed Nylon-6 depolymerization to caprolactam to 55 mol % yield in 6 h, a mixture of [PP13][$NTf_2$] and DMAP was able to improve the depolymerization yield to 86 mol % yield under the same conditions (Figure 4a).[129]

The capacity of ILs to simultaneously solubilize organic and nonorganic species also has been of great interest for chemical recycling by enabling efficient interactions between ionic or metallic catalysts and end-of-life polymers. For example, zinc oxide nanoparticles in [$NBu_4$][Cl] are capable of quantitively depolymerizing PC to BPA in 7 h at 100 °C (Figure 4b); in this reaction, the IL likely acts as a basic cocatalyst.[144] Similarly, [Emim][Ac] can solubilize cobalt chloride and niobium pentoxide catalysts to deconstruct lignin into a variety of commercially useful aromatic compounds, including vanillin, guaiacol, and syringol.[145]

Combining ILs with highly acidic cocatalysts offers a pathway to enhance deconstruction by harnessing Brønsted superacidity.[146,147] A notable example of this behavior is the cracking of low- and high-density polyethylene (LDPE, HDPE) by chloroaluminate(III)-based ILs.[132] These ILs in conjunction with acidic cocatalysts like sulfuric acid were capable of deconstructing LDPE and HDPE into low molecular weight hydrocarbons, including propane, butane, and methylbutane.[132] PE was powdered to increase surface area and enhance deconstruction kinetics, and efficient stirring was required above 180 °C to disperse molten polyethylene within the IL milieu.[132] The study further identified reaction temperature as a handle to influence product composition by achieving greater yields of high activation energy products at elevated temperatures. Hydrocarbon products were obtained in 60−95 wt % yields and separated by solvent extraction, offering a pathway to reuse the IL.[132]

Finally, enzyme-mediated deconstruction is an emerging area of advanced recycling that exploits the high selectivity of enzymes to convert polymers into desirable small-molecule species. ILs are particularly useful in enzyme-mediated deconstruction due to the ability of ILs to solubilize or swell a breadth of species.[148,149] This feature is especially useful for biopolymers that are recalcitrant in the aqueous milieu typically needed for enzyme catalysis. For example, [Emim][Ac] can efficiently extract lignin from cellulose; this cellulose is then enzymatically digestible in the IL.[150] Similarly, the unreactive nature of lignin in water makes it challenging to deconstruct enzymatically in aqueous media. Biocompatible ILs such as [Ch][Gly] can overcome this obstacle by concomitantly solubilizing lignin and enabling the enzymatic deconstruction of lignin to low-molecular-weight products (Figure 4c).[151]

## ■ ILS MAY LOWER THE ENVIRONMENTAL IMPACTS OF ADVANCED RECYCLING

The use of ILs in advanced recycling can lower the environmental impacts of polymer deconstruction relative to neat or organic-solvent-mediated systems if the recycling process is designed to fully recover the ILs after deconstruction. In this section, we describe the features of ILs that offer improvements in IL implementation over common chemical recycling methods, discuss strategies to reclaim ILs from deconstruction processes, and examine environmental challenges that must be addressed when using ILs for deconstructions at scale.

A key challenge in pyrolytic and solvent-based deconstructions is the need for extensive energy input to reach deconstruction temperatures and pressures (whether at high pressure to assist deconstruction or under vacuum to prevent byproduct formation).[152] ILs can enable significant energy savings by facilitating deconstruction under more benign conditions. For example, IL catalytic behavior has been demonstrated to depolymerize epoxy thermosets and carbon fiber epoxy composites at 150 °C and atmospheric pressure,[153] versus the 350−500 °C temperatures and 120−325 atm pressures typical of analogous solvent-mediated approaches.[154,155] With improvements in IL design, more examples of IL-mediated room-temperature deconstructions


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may be realized, as seen in the recent deconstruction of lignin to vanillin at 10−20 wt % yields in metal-containing ILs.[152,156]

The release of solvents from industrial processes is estimated to result in 60% of global industrial emissions and 30% of VOC emissions.[157] Incorporating ILs in place of more volatile solvents for industrial processes, including in deconstruction methods, offers a pathway toward offsetting this environmental impact.[103,158] ILs can be designed for deconstructions to this end to minimize IL-derived environmental impact; for example, shortening alkyl chains in IL cations increases an IL's boiling point, and anion selection can modulate IL boiling points over 100 °C for equivalent cations.[102,159]

In 2018, an imidazolium-based IL was discovered in soil samples near a landfill in the United Kingdom that could trigger an autoimmune chronic liver disease by replacing biological components of mitochondrial proteins.[160] IL toxicity is not yet well characterized, but emerging understanding about the hazards of ILs to animal and human health suggests the need for safeguards to prevent environmental release.[160−162] To highlight some significant findings to date, imidazolium-based ILs are acutely toxic to bacteria at concentrations well below those of molecular solvents,[161] and ILs have been linked to injury among several bacterial and aquatic species.[162] ILs generally exhibit limited biodegradability and high water solubility, which enables their transport to, and persistence in, drinking water reservoirs.[161,163] As a result, ILs have shown some similarities to perfluoroalkyl substances.[163] Many commonplace ILs also rely on toxic or corrosive chemicals for sourcing counterions. For example, fluorinated anions used widely in IL design may be derived from highly reactive superacids that are obtained through hazardous syntheses (e.g., HF chemistry).[164] Such fluorinated anions in ILs demonstrate limited pathways for environmental decomposition and may have significant cytotoxicity.[165,166]

As the increasing use of ILs across applications, including polymer deconstructions, may lead to intentional or unintentional environmental discharges,[167] future IL design should consider environmental impacts and methods for biodegradation as a parameter of research. These developments may work in tandem with the sourcing of IL components from sustainable feedstocks. For example, the design of ILs from renewable organic compounds (e.g., amino acids, citric acid, acetic acid) and nontoxic minerals may help overcome negative IL environmental impacts.[168−170] Further research should also elucidate IL chemistries that can minimize toxicity while meeting performance requirements for targeted applications.[171,172] In the meantime, it is imperative that ILs used in polymer deconstructions are fully contained within the engineering system and separated from the resulting products to enable complete reuse.

To this end, two separation methods dominate in the literature for isolating ILs from monomers and small molecules from deconstruction: distillation and liquid−liquid extraction. Distillation harnesses the low vapor pressures of ILs to evaporate molecular products from the deconstruction reaction vessels. This strategy has the secondary benefit of driving reaction equilibria toward small-molecule species by actively removing the volatile deconstruction products as they are formed. Distillation for product recovery has been demonstrated in the deconstruction of polyesters[105] and nylons,[88] among others. In contrast, liquid−liquid extraction relies on the preferential dissolution of ILs into water over molecular organic solvents to separate ILs and organic products into aqueous and organic phases, respectively. These phases are then concentrated to remove the solvents and recover the dissolved IL and small-molecule products. It is worth noting that the need to distill solvents to reclaim components after liquid−liquid separation may require a higher net energy input than directly distilling deconstruction products from an IL; differences in energy demands between the two strategies could be revealed by a process model combined with life-cycle analysis to evaluate impacts for a specific polymer deconstruction.[173] Liquid−liquid extraction for small molecule recovery from ILs has been shown for, e.g., Nylon-6 and lignin.[174,175]

Advances in IL design and separation techniques may prove useful for the translation of IL-mediated polymer deconstructions to more polymer species or lower energetic costs. For example, recently developed solubility-switchable ILs may become of interest for expanding the library of targetable polymers. These ILs are capable of undergoing a simple, reversible chemical reaction (e.g., protection−deprotection reaction) that induces a marked shift in an IL's hydrophilicity.[114,174,176,177] Such ILs could be harnessed to solubilize and depolymerize hydrophobic plastics, undergo a switching reaction to become hydrophilic, and then be separated from the small-molecule products via liquid−liquid extraction. Membrane separation, crystallization, electrodialysis, and adsorption also have been demonstrated as potential options for IL recovery and may find future use in deconstruction processes.[178,179]

Historically, a mismatch between the attributes of interest for laboratory-scale IL study and industrial-scale IL deployment have limited the translation of ILs to commercial practice.[180] For example, high IL viscosities, limited IL material-property and environmental impact data, and substantial IL raw material costs have hindered the development of IL-based processes.[180] While this Viewpoint has addressed several of these considerations for IL-mediated polymer deconstructions—e.g., lowered IL viscosities at elevated temperatures relevant to deconstructions, strategies to separate monomers from ILs for recyclability, chemical motifs to enhance thermal stability—further effort is needed to tackle outstanding concerns for IL use at a commercial scale. Continued investigations into IL toxicity will be needed for regulatory approval, and ongoing IL chemistry development will be needed to reduce IL costs for batch reactions.[180,181] Technoeconomic analysis is also important to validate the utility of ILs in industrial unit operations by identifying savings arising from IL recyclability and opportunities for process intensification.[173] Additionally, learnings from ongoing pilots of IL-based systems will undoubtedly inform future considerations for IL design and implementation.[181]

ILs overcome significant environmental challenges in polymer chemical recycling by lowering energy inputs to achieve deconstruction and minimizing VOC release by replacing volatile molecular solvents. However, the persistence of ILs in aquatic environments and emerging concerns about IL toxicity to biotic health underscore the need to appropriately contain ILs in deconstruction setups and prioritize environmental considerations in future IL design. Methods to separate ILs from deconstruction products, therefore, become critical in recovering and reusing ILs to prevent environmental leakage while enabling circular life cycles.


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## CONCLUSIONS

ILs offer broad utility for the deconstruction of plastics and biopolymers for chemical and advanced recycling and upcycling. Control over IL chemical design enables the customization of physicochemical properties to target catalytic performance, decomposition temperatures, and polymer solubilities for specific deconstruction applications. This bottom-up control in turn governs deconstruction yields and kinetics, cocatalysis, and facile separation of resulting products from ILs. Recent advances in IL design show promise for efficient deconstructions at lower energy demands than many existing strategies, yet pressing challenges in the environmental impact upon leakage and thermal decomposition should be addressed to facilitate the widespread implementation of ILs in chemical recycling. In short, ILs may find application as a cornerstone of circular polymer economies with continued research and development.

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## ABBREVIATIONS

BPA, bisphenol A; [Bmim][$BF_4$], 1-butyl-3-methylimidazolium tetrafluoroborate; [Bmim][$NTf_2$], 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide; [Bmim][$FeCl_4$], 1-butyl-3-methylimidazolium tetrachloroferrate; [Bmim][$HSO_4$], 1-butyl-3-methylimidazolium hydrogen sulfate; [Bmim][$PF_6$], 1-butyl-3-methylimidazolium hexafluorophosphate; [Bmim][$ZnCl_3$], 1-butyl-3-methylimidazolium trichlorozincate; [$C_3SO_3$Hmim][$HSO_4$], 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate; [Ch][Ac], cholinium acetate; [Ch][Ala], cholinium alanate; [Ch][Cl], cholinium chloride; [Ch][Gly], cholinium glycinate; [Ch][Lys], cholinium lysinate; DMAP, dimethylaminopyridine; [Emim][Ac], 1-ethyl-3-methylimidazolium acetate; [Emim][$AlCl_4$], 1-ethyl-3-methylimidazolium tetrachloroaluminate; [Emim][Cl], 1-ethyl-3-methylimidazolium chloride; [Emim][$NTf_2$], 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide; [HDBU], 8-hydrogen-1,8-diazabicyclo[5.4.0]-undec-7-enium; HDPE, high-density polyethylene; [Hmim][LAc], 1-methylimidazolium lactate; [HTEA][LAc], triethylammonium lactate; IL, ionic liquid; LDPE, low-density polyethylene; [$NBu_4$][Cl], tetrabutylammonium chloride; PC, polycarbonate; PET, poly(ethylene terephthalate); PHB, poly(3-hydroxybutryate); [PP13][$NTf_2$], *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane)sulfonimide; TGA, thermogravimetric analysis; VOC, volatile organic compound

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