# Depolymerizing PET via "Imidazolysis" for Obtaining a Diverse Array of Intermediates from Plastic Waste

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**Abstract**:

Polyethylene terephthalate (PET) is a ubiquitous commodity plastic used in applications including textiles, food packaging, drink bottles, and thermoplastic resins. Like other synthetic polymers, the massive accumulation of PET on Earth's surface has presented formidable environmental challenges. As a polyester, PET is susceptible to chain cleavage (i.e., depolymerization) via various "chemolysis" methods. Here, we introduce a approach to PET cleavage by imidazole (and related compounds): "imidazolysis". Reacting PET with excess imidazole yields 1,1'-terephthaloylbisimidazole (TBI) which can be further transformed into an array of small products such as amides, benzimidazoles, and esters, or potentially used as monomers for polymers. The TBI molecules obtained via imidazolysis are versatile intermediates (owing to their activated carbonyl groups) which can be stored and subsequently converted to specific final products later. This means that the target product(s) do not have to be predetermined when the depolymerization reaction is carried out, and this methodology could provide flexibility to meet demands for various chemical products based on the terephthalic acid (or p-xylene) motif. Imidazolysis may also be of broad utility in depolymerizing other polyesters as well as polyurethanes (PU).

**Keywords**: Poly(ethylene terephthalate), Depolymerization, Aminolysis, Imidazole, Plastic waste

## 1. Introduction

The practice of recycling synthetic plastics is perceived to be a socially responsible task in modern times as it plays a crucial role in collecting useful materials, combatting environmental pollution, and conserving petroleum reserves. However, the majority of plastics are still either landfilled or incinerated.

The commercial and household consumption of poly(ethylene terephthalate) (PET) has experienced significant growth in recent decades, particularly from the production of bottles and containers for food, drinks, and personal care products, as well as for texttile fibers, and other consumer goods.[1] The widespread adoption of PET can be attributed to its exceptional durability, gas barrier properties, cost-effectiveness, minimal need for processing additives, etc.[2] PET has an annual global production of ~70 Mton, with 71% of this production dedicated to plastic bottle manufacturing.[3-5] While there is a well-established collection and sorting infrastructure for handling post-consumer PET,[6] the overall recycling rate for PET waste remains relatively low, averaging ~29% in the United States.[7]

The simplest approach to recycling plastic is through thermomechanical processing; however, this is better considered to be "downcycling" as it detrimentally affects polymer properties, yielding materials with fewer uses and less value than "virgin" plastics.[8] Because of these challenges, chemical recycling of plastics (i.e., depolymerization) has gained significant interest since it targets reducing waste while still taking advantage of the chemistry of plastics.[9] Notably, PET is the only condensation polymer among the plastics stamped with resin identification codes (RIC) 1-6. PET, and more generally, the polyalkylene terephthalate (PAT) family are polyesters that are susceptible to attack/degradation via "chemolysis" with various reagents.

Thus far, significant advancements have been made in the depolymerization and partial chemical modification of PET through chemolysis methods, including hydrolysis (water),[10, 11] alcoholysis (alcohols),[12, 13] glycolysis (ethylene glycol),[9, 14, 15] aminolysis (amines),[5, 8, 16] and ammonolysis (ammonia).[9, 17] Each technique involves chemically cleaving an ester bond with the corresponding nucleophile, leading to the formation of C-O or C-N bonds.

Some chemolysis approaches to PET are targeted at recovering essential building blocks for the synthesis of fresh PET such as dimethyl terephthalate (DMT). DMT is obtained through alcoholysis with MeOH. Recovery of terephthalic acid (TA) can be achieved via hydrolysis.[10, 13] Furthermore, the glycolysis of PET to bis-2-hydroxyethyl terephthalate (BHET) has already been successfully implemented on an industrial scale.[18, 19] In recent years, aminolysis has emerged as a rapid and economical method for PET depolymerization, owing to the more reactive nature of amines, as the conversion of esters to amides can occur even at ambient temperature. For example, the quantitative depolymerization of PET by primary (1°) amines or amino alcohols such as monoethanolamine (MEA) can be carried out at ambient temperature in the absence of a cosolvent using sufficient molar excess (e.g., 20 eq.) of the amine yielding terephthalamide diols. Low to moderate molecular weight poly(ester-amide)s have been successfully synthesized from these terephthalamide diols at lab-scale quantities (**Figure 1a**), and they have utility as biodegradable polymers in tissue engineering.[8, 16, 20, 21] However, broader applications for small terephthalmide molecules (e.g., *N,N'*-dibutylterephthalamide) have not yet emerged.

In collaboration with Demarteau and Sardon, our group has previously reported the aminolysis of PET using 1-(3-aminopropyl)imidazole (API), yielding a bis-imidazole terephthalamide (**Figure 1b**), which we had previously synthesized using API and terephthaloyl chloride in acetonitrile ($CH_3CN$) with potassium carbonate ($K_2CO_3$) as a base.[22] This product was used to synthesize imidazolium polyamide-ionenes, which have intrinsic and rapid self-healing properties and are highly amenable to 3D printing.[22, 23]

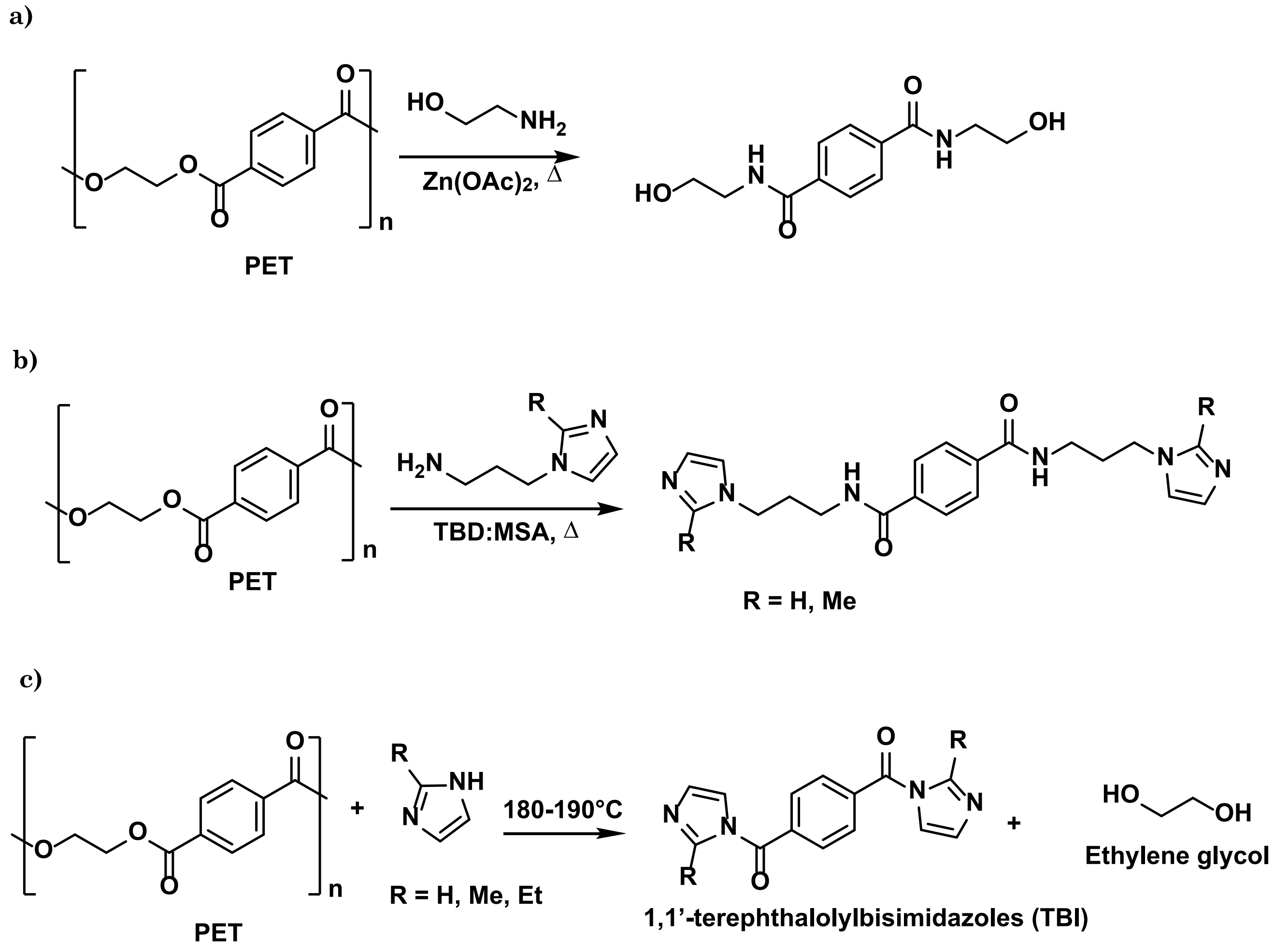


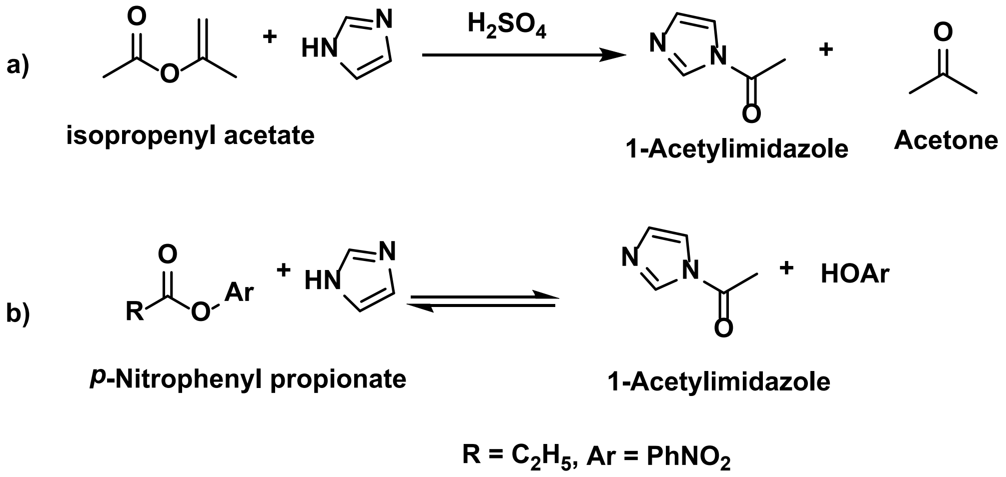
**Figure 1:** Examples of products formed via aminolysis of PET a) with MEA; b) with API that can be used in the synthesis of imidazolium ionenes and c) expected TBI products of depolymerization of PET by imidazoles.

It is worth noting that the depolymerization of PET by API is still a classical aminolysis of an ester; the imidazole moiety did not participate in the reaction. However, that work has led us to consider whether imidazole itself might be able to depolymerize PET via "imidazolysis". Imidazole is conventionally represented as having both secondary (2°) and tertiary (3°) amines within the 5-membered heterocycle, although the true structure is a tautomer.[24, 25] As such, imidazole and its analogs such as 2-methylimidazole, 4-methylimidazole, etc., are essentially 2° and 3° amine hybrids and thus should be able to cleave esters forming 1,1'-terephthalolylbisimidazoles (TBIs, **Figure 1c**) while 1-methylimidazole (N-methylimidazole) would not.

Imidazole and its derivatives find use in both natural and synthetic organic chemistry. Imidazole moieties are found in pharmaceuticals (e.g., miconazole, clotrimazole), fungicides (e.g., prochloraz) and biologically significant compounds (e.g., histidine, an essential amino acid).[26, 27] Imidazole is also a building block for N-alkylimidazoles,[28] imidazolium ionic liquids (ILs), ionic polymers. The versatility of imidazoles for organic synthesis arises from the ability to create heterocycles with many different substituents on the N and/or C atoms within the 5-membered ring.[25, 29-31] A recent work has demonstrated the role of imidazoles as a catalyst in obtaining a reaction intermediate which enhances the selective depolymerization of bisphenol A-based polycarbonate (BPA-PC) into valuable cyclic complex carbonates and BPA under mild condition.[32]

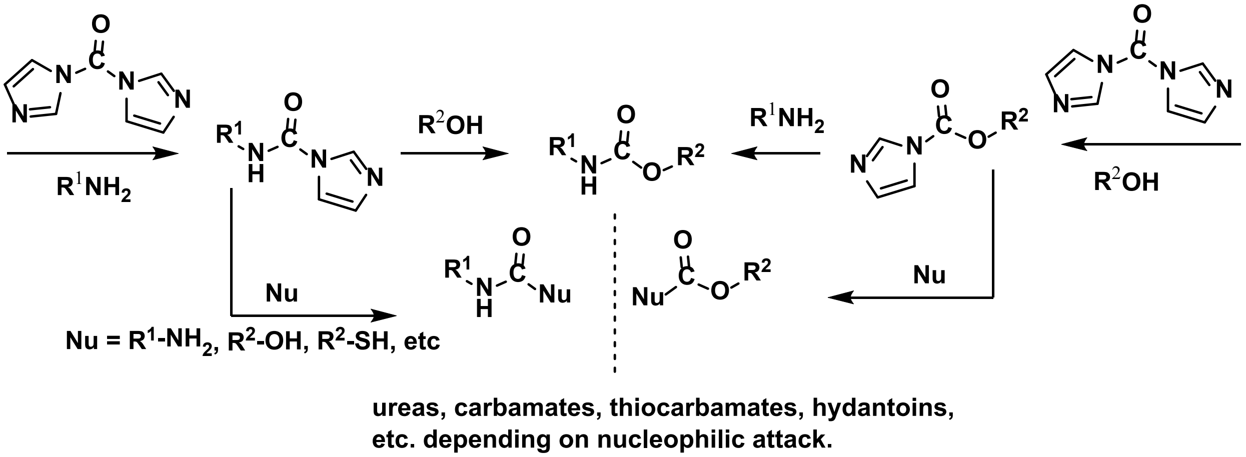
In this report, we discuss the results of the utility of imidazole compounds in depolymerizing PET and the subsequent reactions of those products to form small molecules. During the preparation of this manuscript, we searched SciFinder$^n$ for the term "imidazolysis," which yielded a total of 9 results, with publication dates ranging from 1959 to 2003. In 1952, Boyer reported on the acetylation of imidazole via acid ($H^+$) catalyzed reaction with isopropenyl acetate but did not use the term "imidazolysis". **Scheme 1a** illustrates how the final product was balanced by the enol to keto tautomerization from reactant to acetone, except for another product, "1-acetylimidazole" in this reaction.[33] In 1998, Schmeer investigated the imidazolysis of esters in the presence of different solvents (water, acetonitrile, 1,4-dioxane, and propylene carbonate, etc.); where the formation of tetrahedral zwitterionic as an intermediate which later dissociates into two different routes (**Figure S1**).[34] Later, in 1977, Rivetti and Tonellato further investigated the imidazolysis of esters in benzene. They used an equimolar solution of *p*-nitrophenyl propionate (PNPP) and imidazole, which resulted in a reversible reaction at room temperature (**Scheme 1b**).[35] However, we did not find imidazolysis of small diesters in the existing literature.

**Scheme 1:** Previously reported examples of a) "acetylation of imidazole" and b) "imidazolysis in benzene" of small molecule esters.



Herein, we report for the first time the quantitative depolymerization of PET (or any polyester) via imidazolysis. In this study, imidazolysis was performed without a cosolvent, as the melting points of the imidazole compounds are sufficiently low to serve as both reactant and solvent. The obtained symmetric TBI products are connected to the broader family of N-acyl imidazoles (**Scheme 2**), which are well-known exclusive electrophiles that exhibit tunable reactivity and chemical selectivity towards forming esters and amides favoring nucleophilic substitution reactions.[36, 37]

**Scheme 2:** Typical reaction to form N-acylimidazole intermediates and their subsequent reactions.



N-acylimidazoles are generally produced from N,N-carbonyldiimidazole (CDI), which itself is typically obtained via the reaction of excess imidazole with phosgene ($COCl_2$). CDI is commonly used for coupling amino acids for peptide synthesis but has also been demonstrated to be useful a functionality within polymer science for synthesizing urethane and urea-containing monomers, as explained in **Scheme 2**.[38, 39]

Staab has already reviewed the importance of azolides (N-heterocyclic amides, e.g., CDI, N-acylimidazoles) of carbonic acid derivatives in transacylation reactions, where the high degree of reactivity of azolides results from the quasi-aromatic nature of azoles.[40] Following these, diimidazolides or TBIs can also show equivalent performance. Therefore, the molecules obtained via imidazolysis of PET (and likely other polyesters) are sufficiently reactive to provide a versatile platform to generate amides and esters based on the choice of amines and alcohols, respectively (**Scheme 3**). The TBIs derived from waste PET are functionally equivalent to terephthaloyl chloride or terephthalaldehyde. Thus they can be used to obtain small molecules like bisbenzimidazoles, diamides, diesters, and imidazolines/oxazolines,[22, 31] and potentially polymers.

These findings underscore the ability of “imidazolysis” as a means of developing intermediates with enhanced properties and promote a circular economy for plastic materials.

## 2. Experimental

### 2.1. Materials

Imidazole (99%) and o-Phenylenediamine (*o*-PDA, 99%) were purchased from Beantown Chemical (Hudson, NH, USA). Polyphosphoric acid (PPA, > 85%), Phosphoric acid ($H_3PO_4$, 99%), and 2-Ethylimidazole (99%) were purchased from Thermo Scientific (Waltham, MA, USA). 2-Ethyl-4-Methylimidazole (96.82%) was purchased from Chem-Impex Int’l Inc. (Wood Dale, IL, USA). 2-Isopropylimidazole (98%) and 4-Methylimidazole (>98%) was purchased from Tokyo Chemical Industry Co., Ltd (Portland, OR, USA). 2-Phenylimidazole (>98%), n-Butylamine (99%), and 2-Methylimidazole (97%) were purchased from Alfa Aesar (Ward Hill, MA, USA). All these chemicals were used as received except *o*-PDA, which was recrystallized prior to use. Acetonitrile (ACN), Tetrahydrofuran (THF), and Acetone were used as solvents and purchased from VWR. 2,4,5-Trimethylimidazole was previously synthesized in our laboratory according to a published method. [41]

### 2.2. Experimental procedure

Post-consumer PET bottles were collected and thoroughly washed with soapy water, followed by thorough rinsing with deionized water. Acetone was then used to remove any remaining surface contaminants. PET bottles were manually cut into 5-6 mm flakes and dried in an oven at 70 °C overnight. The depolymerization reactions were initially performed at small scales (e.g., 2 g PET (10.4 mmol), 5.6 g imidazole (83.2 mmol)) in a microwave synthesis reactor (MCR). A predetermined weight of PET (pellets/flakes) and 8 eq. of imidazole (per PET repeat unit) were thoroughly homogenized together via grinding (IKA Multidrive Control) before loading the mixture into a 30 mL microwave reaction vial. This co-grinding of PET + imidazole was found to yield much more consistent results as the PET and imidazole were already in intimate contact prior to heating. A Monowave 400 microwave reactor (Anton Paar GmbH, 1600 VA, 850 W maximum magnetron power output) was used with temperature, time, and stirring speed control (**Figure S2**). PET depolymerization with selected imidazole derivatives (e.g., imidazole, 2-methylimidazole) was also successfully scaled up (e.g., 35 g PET with 110 g imidazole) in a 250 mL heavy-walled round-bottom pressure vessel (Ace Glass).

The disappearance of the PET particles was visually monitored, and heating was continued until the mixture became homogenous. After this, the reaction mixture was allowed to cool to room temperature overnight. ACN was added to the crude mixture, allowing for the removal of any possible remaining PET oligomers, excess imidazole, and the produced ethylene glycol (EG). The TBI products were insoluble in ACN, and this allowed for them to be collected via vacuum filtration, where they were washed with THF. The TBI products were off-white or greyish solid powders for compounds 1b to 4b and yellowish to dark brown solid powders for compounds 5b to 8b (**Figure S3**). These products were dried under vacuum at 75 °C overnight.

## 3. Computational methods

Density functional theory (DFT) calculations were used to analyze the electrostatic potential (ESP) features of the imidazole molecules in the gas phase; explicitly, we evaluated PET-Imidazole (SM1), PET-2-Methyl-imidazole (SM2), PET-3-Methyl-imidazole (SM3), and (1H-imidazol-1-yl)(phenyl)methanone (SM4). Initially, 40 different conformers were generated using the generic algorithm of OpenBabel,[42] followed by geometric optimization using the B3LYP functional[43, 44] and a 6-31(d) basis set.[45, 46] Each of the lowest energy conformers was selected for further electrostatic surface potential (ESP) and Conceptual Density Functional Theory (CDFT) analyses.[47-50] To do this, a single point energy calculation of the chosen conformer was conducted using a 6-31++(d,p) basis set,[51] along with DFT-D3 dispersion corrections.[52] The Multiwfn package[53] was used to calculate the ESP and general interaction properties functions (GIPFs).[54-56] The GIPFs were determined utilizing van der Waals surfaces and an electron density isosurface of 0.001 e/Bohr$^3$.[55] Based on this approach, we obtained the molecular volume ($V_m$), surface area ($SA$), minimum ESP value ($V_{min}$), maximum ESP value ($V_{max}$), average ESP value ($\bar{V}$), and molecular polar index ($MPI$) of each molecule.

To further analyze the chemical stability of the evaluated molecules, CDFT properties such as the vertical ionization potential (VIP), vertical electron affinity (VEA), Mulliken electronegativity ($\chi$), chemical potential ($\mu$), hardness ($\eta$), softness ($\eta^{-1}$), and Parr's electrophilicity index ($\omega$) were calculated using the wave function of N, N-1, and N+1 electron states, in which N is the number of electrons corresponding to the neutral molecule. In our approach, CDFT properties were also calculated using the Multiwfn package, and the single-point energy calculations were performed using the 6-31++(d,p) basis set and DFT-D3 dispersion corrections. Finally, we inferred the relative N-C bond strength by carrying out incremental scans corresponding to different fixed bond lengths, in which the energy of each conformer is plotted as a function of the distance between the C and N bonded sites, carried out using the same level of theory described above with an increment spacing of 0.1 Å. All DFT calculations were performed using Gaussian 09.[57]

## 4. Results and Discussion

### 4.1 Depolymerization of PET via Imidazolysis

Imidazole itself, along with alkyl or aryl-substituents at the 2, 4, and/or 5 positions, are comparable to heterocyclic 2° amines, exhibiting moderate basicity ($pK_a$ = 7 to 8.92) (**Table 2**) and are able to undergo nucleophilic N-substitution reactions with esters, as depicted in **Scheme 3 and Figure 1(c)**. This study screened the depolymerization of PET via imidazolysis using eight different imidazoles shown in **Table 1** and their comparative reactivity toward forming the corresponding symmetric TBI compounds.

**Scheme 3:** Depolymerization of PET by imidazole and subsequent upcycling to terephthalamide and terephthalate products.

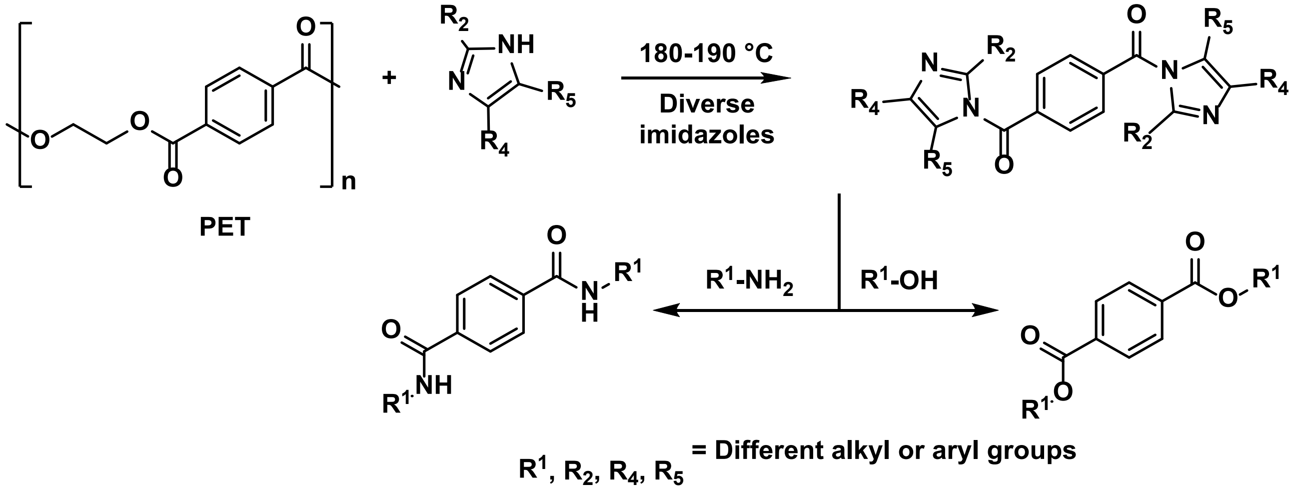
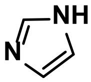
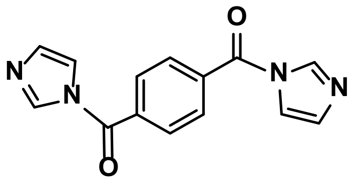
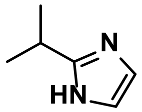
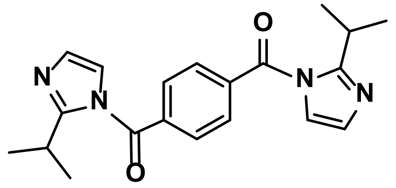
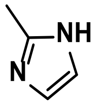
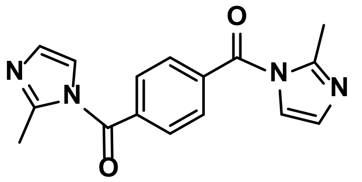
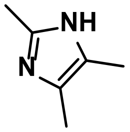
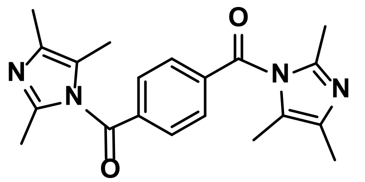
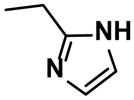
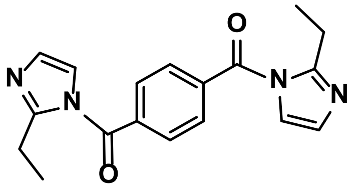
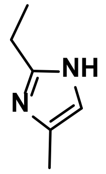
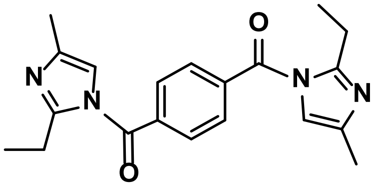
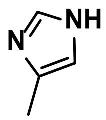
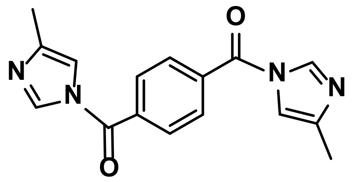
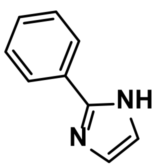
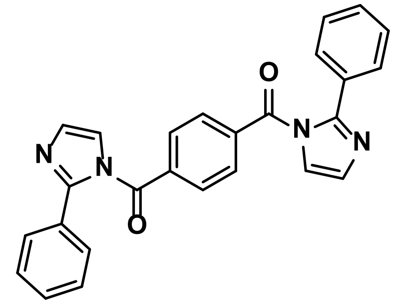


**Table 1:** Imidazole reagents used, and corresponding products obtained via imidazolysis of PET.

| Reagent | Product | Reagent | Product |
|---|---|---|---|
| <br>Imidazole<br>1a | <br>1b | <br>2-Isopropyl imidazole<br>5a | <br>5b |
| <br>2-Methyl imidazole<br>2a | <br>2b | <br>2,4,5-Trimethyl imidazole<br>6a | <br>6b |
| <br>2-Ethyl imidazole<br>3a | <br>3b | <br>2-Ethyl-4-methyl imidazole<br>7a | <br>7b |
| <br>4-Methyl imidazole<br>4a | <br>4b | <br>2-Phenyl imidazole<br>8a | <br>8b |

Imidazole, possessing moderate basicity ($pK_a$ ~7)[58], was first monitored in reaction with PET at 180 °C. Over a duration of 80 min, all of the PET particles completely disappeared, with a recovered yield of 61% of 1,1'-(1,4-Phenylene)bis[1-(1H-imidazol-1-yl)methanone] ("TBI", 1b). The product was verified by $^{1}$H NMR (**Figure S4**) and $^{13}$C NMR (**Figure S5**) spectra.

Given the success with imidazole, reactions with imidazole derivatives bearing a single alkyl substituent were then considered (2a-5a). The presence of electron-donating (e.g., -Me, -Et) groups on the imidazole ring resulted in faster reactions. It has been established in prior findings that the basicity of amines is highly correlated with their reactivity in amidation reactions with esters.[16] As such, we obtained a more substantial yield (95%) of product 2b, which suggests 2-methylimidazole is a more effective imidazolysis reagent for PET depolymerization. This correlates with the larger $pK_a$ of 2-methylimidazole ($pK_a = 8.1$). However, it is worth noting that the melting point of 2-methylimidazole ($T_m = 142\ ^oC$) is significantly higher than that of imidazole ($T_m = 86\ ^oC$) such that the reaction was run at a slightly increased temperature (190 ºC) primarily to reduce viscosity. Reactions of PET with 3a and 4a were also successful in obtaining TBIs with acceptable yields (see **Table 2)**. The imidazolysis of PET with 2-isopropylimidazole (5a) was also attempted but was found to have a lower yield despite the stronger basicity of 5a than imidazole. One possible reason could be the steric hindrance caused by the isopropyl group at the same position, affecting the progress of the reaction even at 190 °C. These characteristics are also reflected in the solubility of product 5b with common organic solvents (**Table S1**). NMR characterizations of these molecules are provided in **Figures S6-S13.**

**Table 2:** Parameters for imidazolysis reactions of PET and yield of recovered product.

| Entry[a] | Imidazole | $T_m$ (°C)[b] | $pK_a$[58] | Product | Depolymerization (MCR data) | | | Yield[d] (%) |
|---|---|---|---|---|---|---|---|---|
| | | | | | Temp (°C) | Time (min) | Yield[c] (%) | |
| 1 | Imidazole (1a) | 85-92 | 7 | 1b | 180 | 80 | 61 | 82 |
| 2 | 2-Methyl-imidazole (2a) | 142-144 | 7.85-8.10 | 2b | 190 | 60 | 70 | 95 |
| 3 | 2-Ethyl-imidazole (3a) | 78-81 | 7.99-8 | 3b | 180 | 80 | 66 | 71 |
| 4 | 4-Methyl-imidazole (4a) | 44-47 | 7.69-7.80 | 4b | 180 | 90 | 39 | 65 |
| 5 | 2-Isopropyl-imidazole (5a) | 129-131 | 7.97 | 5b | 190 | 100 | 38 | – |
| 6 | 2,4,5-Trimethylimidazole (6a) | 65[d] | 8.92[59] | 6b | 60 | 60 | 72 | – |
| 7 | 2-Ethyl 4-methyl imidazole (7a) | 47-54 | 8.68 | 7b | 190 | 135 | 34 | 60 |
| 8 | 2-Phenyl-imidazole (8a) | 142-148 | 6.44[60] | 8b | 180 | 120 | 32 | 59 |

b= Melting point according to consumer product, c = yield obtained by pressure vessel reaction, d = determined in the lab

[a] 2g PET and 8 eq. (in mole) of imidazole were used for microwave reaction. 10g PET with 8 eq. of imidazole compounds was used for upscaling in a pressure vessel reaction (For reagent 1a, PET was taken as 35g).

Considering that the basicity of imidazole can be influenced/enhanced by the position and size of alkyl groups on the C(2), C(4), and/or C(5) positions of the imidazole ring structure, di- and tri-alkyl-substituted reagents were also tested (6a, 7a).[58] With these compounds, some variation in reaction parameters was required to achieve depolymerization, although each has a comparable basicity (**Table 2**). Product 6b was obtained at 180 °C with the shortest reaction time (30 min) and a good yield (72%), which can be attributed to the high nucleophilicity of 2,4,5-trimethylimidazole (6a) ($pK_a = 8.92$). It is worth noting that an exception was observed for 2-ethyl-4-methylimidazole (7a), as the imidazolysis of PET proceeded slowly even at 190 °C, taking almost 2.5 h to complete in the microwave reactor. Similar to 5a, it is hypothesized that the steric bulk of 7a could lead to poor interaction with PET flakes, making it an ineffective reagent for depolymerization, and one additional cause might be its lower basicity ($pK_a = 8.68$) compared to 6a. The presence of all these monomers had been confirmed by $^1H$ and $^{13}C$ NMR (**Figures S14-S17**).

Finally, 2-phenylimidazole (8a) was considered for the imidazolysis of PET. This compound contains a pendant benzene ring, which has the effect of making it the weakest base ($pK_a = 6.44$) among all of the imidazoles considered. However, it was observed that 8a was able to fully depolymerize PET, although it required 120 min (**Figures S18-S19**). The bulky phenyl group and a high melting point of 8a might be responsible for the slow reaction. It is worth mentioning that product 8b was moderately soluble in typical aromatic organic solvents (e.g., toluene, xylene), distinguishing it from other TBIs (**Table S1**).

The TBI produced (1b–4b) in these reactions exhibits specific solubility (1 mg TBI per mL of solvent) in common alcohols (e.g., MeOH, EtOH) and water, and these solvents do not react with TBI molecules (See **Figures S20, S21 (a)**) at room temperature. The solubility of all the TBI products obtained is provided in **Table S1.**

Overall, these studies show that PET can indeed be depolymerized directly in the melt phase via imidazolysis with different imidazoles, yielding TBI products. The use of a MCR was found to be particularly useful for rapidly screening reagents and reaction conditions before scale-up in sealed pressure vessels. In the MCR, the complete disappearance of PET required between 1.0 - 2.5 h but resulted in a lower yield. This phenomenon aligns with previous studies where fast heating rates in MCR led to incomplete conversion of some starting materials.[61] In contrast, the traditional reaction with larger PET flakes takes a comparatively longer time but results in a higher yield. Although, the steric bulk on some alkyl-substituted imidazoles can require additional time.

A recent study has shown successful depolymerization of PET and other polyesters with morpholine in the presence of a titanium-based catalyst. The morpholine-amide product was then transformed into valuable small molecules via hydrolysis, Grignard reaction, etc. However, even in the presence of a catalyst, the process required 2 d for complete conversion (> 99%).[62] Our study revealed that imidazolysis by conventional heating could make an 82% yield of 1b within a 24 h reaction time without a catalyst. Here, we focused on determining the efficacy of imidazole compounds for the degradation of PET. Future work will consider the possible synergistic effects of catalysts such as TBD:MSA for imidazolysis, which will likely require fewer equivalents of the imidazole compounds and may improve the yields for the bulkier imidazoles.[8, 22] Hydrolyzing waste PET to terephthalic acid (TA) is a valuable practice in promoting plastic circularity and avoiding the reliance on virgin resources. This work successfully converted back TBI products (1b and 2b) into TA via acid-catalyzed hydrolysis using $HCl/H_2SO_4$ as catalysts (**Figure S22 a,b**) in mild conditions.

### 4.1.1 Fourier-transform infrared spectroscopy (FTIR) analysis

Fourier transfer infrared (FTIR) spectra were obtained with a Thermo Fisher Scientific ATR-FTIR with a resolution of 4 $cm^{-1}$ and 128 scans within a spectral region of 4000-400 $cm^{-1}$. The frequency of the depolymerized compounds displays distinct and consistent vibrational peaks, which are noticeably different than PET itself (**Figures 2a, b**). Specifically, the intensity of the sharp ester carbonyl (C=O) peak at 1712 $cm^{-1}$ in PET decreases in all the depolymerized products.

Assigning C=O shifting for TBIs is challenging since these compounds cannot form H-bonds with the adjacent amide molecules and are typically found in the 1670 to 1630 cm$^{-1}$ region.[63, 64]

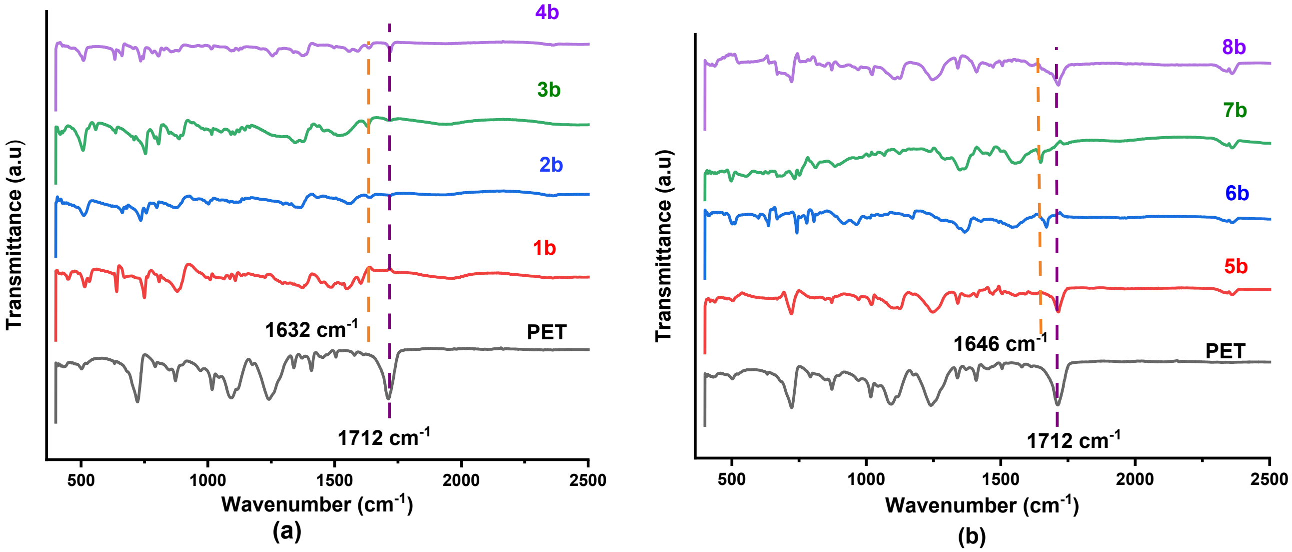


**Figure 2:** FTIR spectra for comparison of depolymerized products with PET a) PET with monomers 1b to 4b b) PET with monomers 5b to 8b.

However, for N-heterocyclic compounds, this absorption band can be shifted at slightly higher frequencies due to the conjugation between the imidazole ring N(1) and the acyl group, compared to C=O groups attached to aliphatic compounds. Consequently, the symmetric stretching of the acyl imidazoles in the degradation products was found in the range of 1712 to 1600 cm$^{-1}$, indicating substitutions happened during the reaction. Additionally, there is no trace of characteristic NH---N bonding of unsubstituted imidazole in the 2800 to 2600 cm$^{-1}$ region, confirming that the TBIs have been formed by the disappearance of the N(1)-H proton. Nevertheless, the spectra still exhibit vibrational frequencies in 1660 to 1450 cm$^{-1}$ bandwidth in the depolymerized compounds, attributable to intramolecular C–N and C–C bonding.[64, 65] The complete FTIR spectra are shown in **Figures S23a, b**.

### 4.1.2 Nuclear magnetic resonance spectroscopy (NMR) Analysis:

A Bruker Avance instrument (Billerica, MA) with 500 MHz was used to collect $^1$H and $^{13}$C NMR spectra in DMSO-$d_6$ for all the TBI products. **Figure S4** shows the product of PET imidazolysis with imidazole (1b) and the requisite proton integrations. The most deshielded resonance peak around $\delta$ 8 ppm is assigned to the benzene ring, verifying identical para-substitution, and the corresponding carbonyl group is observed near $\delta = 170$ ppm in $^{13}$C NMR (**Figure S5)**. Two signals between $\delta = 7 - 8$ ppm are attributed to the symmetrical imidazole C(2), C(4) and C(5)-H atoms.[66] At the same time, the presence of C(2) proton is absent in other depolymerized products having 2-substituted imidazoles, and subsequent alkyl groups were evident between $\delta$ 1 to 3 ppm in $^1$H NMR and at $\delta$ 10 to 30 ppm in $^{13}$C NMR, respectively (see **Figures S6-S19**).

## 5. ESP and CDFT analysis

**Figure 3** shows the optimized conformers, and ESP surfaces for the molecules SM1, SM2, SM3, and SM4, in which the red-colored surfaces represent the higher ESP values, dominated by nuclear effects, and the blue-colored surface regions represent lower values of the ESP, dominated by electron charges. The yellow and blue spheres in **Figure 3** indicate the local maxima and minima on the surface, respectively. Similar ESP surfaces are obtained for SM1, SM2, and SM4; in contrast, the ESP surface of SM3 is dominated by positive values. Overall, the local minima are found around the nitrogen and oxygen sites, while the local maxima are mainly located around hydrogen atoms.

A more quantitative analysis of the ESP is obtained by looking at the GIPF values presented in **Table S2**. SM4 has the smallest $V_m$ and $SA$, followed by SM1, and only minor differences are observed between SM2 and SM3. Consistent with **Figure 3**, SM3 is dominated by a positive potential, as observed by the predicted values of $V_{max}$ and $V_{min}$. The Molecular Polarity Index (MPI) is a good quantitative measure of molecular polarity related to non-uniform charge distributions, in which a higher MPI value indicates greater molecular polarity, which can significantly affect the molecular behavior in the condensed phase. Considering the evaluated molecules, SM3 presents the largest MPI, followed by SM1, SM2, and SM4.

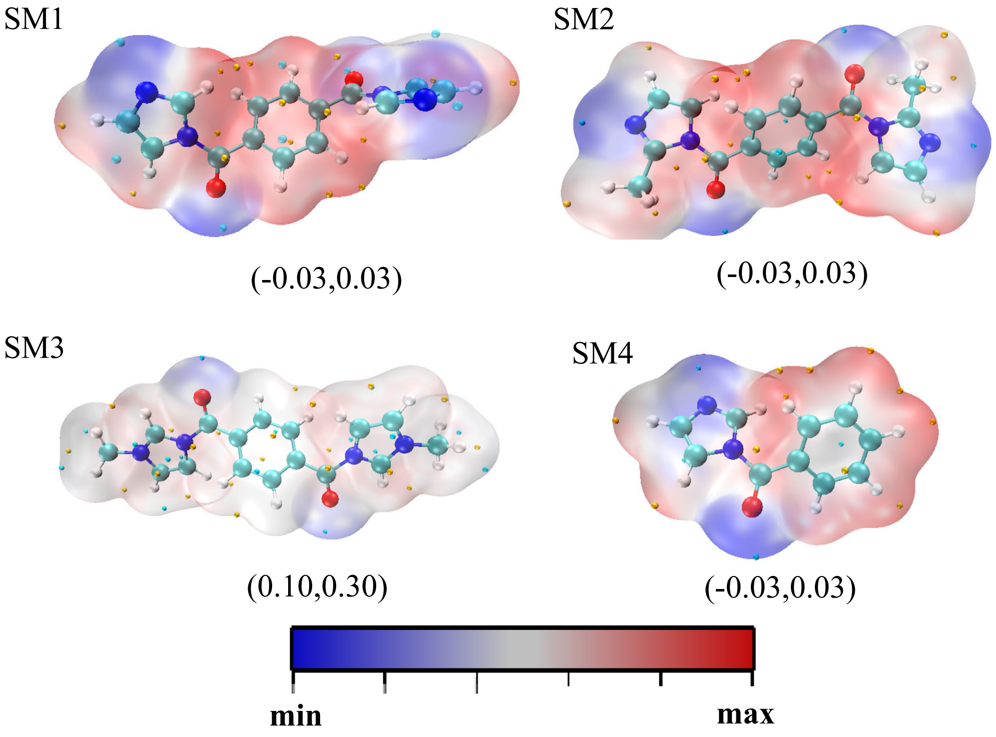


**Figure 3:** ESPs of the evaluated imidazole molecules evaluated at $\rho = 0.001\ e/Bohr^3$, in which the min and max values (a.u. units) are indicated below the respective molecules in parenthesis. Local maxima and minima are identified by the yellow and blue spheres, respectively. Atom color code: cyan = carbon; white = hydrogen; red = oxygen.

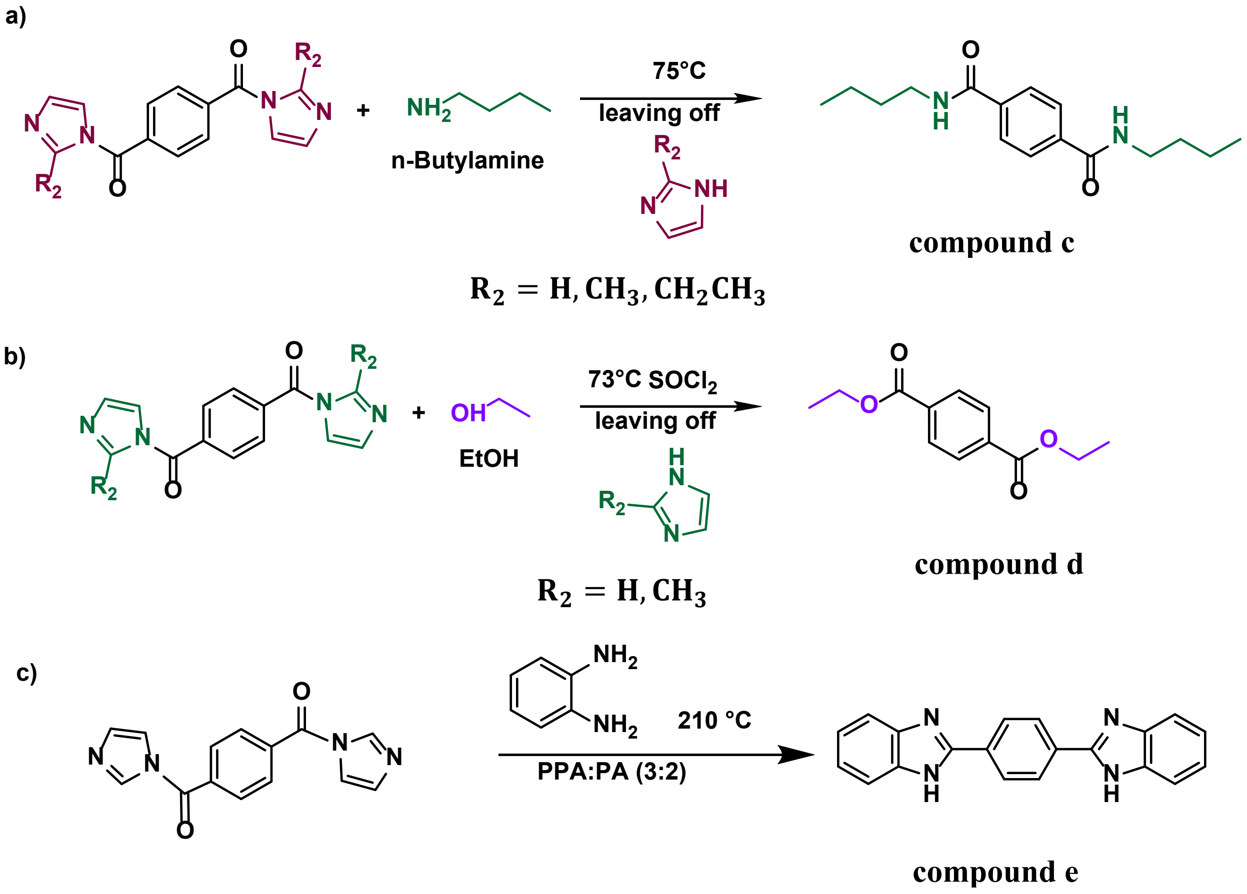
As mentioned before, CDFT properties (summarized in **Table S3**) can be used to infer the reactivity of SM1, SM2, SM3, and SM4. SM3 presented the largest global $\chi$ and $\omega$, related to a stronger electron-molecule interaction and a greater tendency to accept electrons. Considering the polarizability of the molecules, SM4 is found to have the largest $\eta$, followed by SM3, SM1, and SM3. Additional information is provided in **Tables S4-S7**, which include the local electrophilicity index ($\omega^{loc}$), condensed local softness for electrophilic attack ($s^-$), nucleophilic attack ($s^+$), and radical attack ($s^0$), as well as Hirschfeld charges. In general, the O atoms of the evaluated molecules present pronounced $\omega^{loc}$, $s^+$, $s^0$, and more negative charges, suggesting that these sites are more susceptible to nucleophilic and radical attack. Conversely, carbon sites present larger $s^-$ values.

Finally, considering the bond strength of the N-C sites (sites 4 and 6 of SM1-SM3 and sites 4 and 8 of SM4), the optimized conformer bond lengths correspond to 1.413, 1.410, 1.467, and 1.419 Å for SM1, SM2, SM3, and SM4, respectively. This suggests that the SM3 N-C bond is slightly weaker than those of SM1, SM2, and SM3. We explicitly evaluate the conformer energy as a function of the distance between the N and C atoms, with the results summarized in **Figure S24** (the minimum energy value is set to zero). Similar profiles are observed for SM1, SM2, and SM4; however, a broader potential profile is obtained for SM3, suggesting a relatively weaker C-N bond.

## 6. Synthesis of value-added small molecules from TBIs

The reactivity of TBI products obtained by imidazolysis was also considered. The concept of TBIs or "activating" carbonyl bisimidazole compounds can be traced back to Gerngross' pioneering work in 1913 with the preparation of N-benzoylimidazole. Later, significant progress was obtained with the preparation of other acetylimidazoles and most importantly, through the invention of carbonyldiimidazole (CDI), and a solid foundation about the chemistry and reactivity of TBIs had been established by Staab.[67] According to his findings, the acyl-substituted pyrrole-like N(1) in these heterocyclic azolides possesses a lone pair of electrons that can undergo delocalization within the azole-π-system along with the pyridine-like N(3). This delocalization results in a partial positive charge on either N atom and intensifies the electron-withdrawing influence on the C atom of the C=O group. Consequently, the acyl moiety within the azolides becomes highly susceptible to nucleophilic attack.[31] The reactive nature of TBIs obtained from PET have been analyzed via there different methods of reaction as depicted in **Scheme 4**.

**Scheme 4:** Modification of TBIs a) Aminolysis of TBIs with n-butylamine to terephthalamide (compound c), b) Esterification of the TBIs with ethanol to form diethyl terephthalate (compound d), and c) Synthesis of bisbenzimidazole (compound e) reacting with TBI(1b) and *o*-PDA.



### 6.1 Aminolysis of carbonyl bisimidazoles

The transacylation activity of imidazolides or carbonyl diimidazolides has been extensively investigated by previous researchers.[36, 40, 68] Following this, our upcycling study aimed to explore the reactivity of TBIs in aminolysis reactions with excess n-butylamine under reflux. It was observed that all three TBIs (1b, 2b, and 3b) exhibited sufficient reactivity to form the symmetric 2° terephthalamide (compound c) in **Scheme 4a**, with moderate to high yield, as the imidazoles were displaced in favor of amide formation with amines. While TBIs incorporated with alkyl groups (2b and 3b) could be more potent than the simple TBI (1b), they might exhibit less susceptibility towards amidation than 1b, leading to lower yields. Amidation product (c) was obtained from 1b, 2b, and 3b with 86.5%, 74%, and 72.8% yields, respectively. As per the integration with the requisite $^1H$ NMR signals, **Figure S25** indicates that the N-H proton might overlap with the benzene ring around $\delta = 8$ ppm, confirmed by integrating all signal peaks. All the -$CH_2$- $^1H$ NMR signals appear in the range of $\delta = 1.25 - 2.8$ ppm with the terminal -$CH_3$ group at $\delta = 1$ ppm. The $^1H$ and $^{13}C$ NMR spectra of the same product (c) obtained from 2b and 3b can be found in **Figures S26** and **S27.**

### 6.2 Esterification of carbonyl bisimidazoles

The reversion of TBIs to ester products was also considered. It was found that simply adding TBIs to excess alcohol (e.g., MeOH, EtOH, n-BuOH) at room temperature was not sufficient to release the imidazole and form the corresponding esters unless an acid catalyst was used. Prior reports suggested that the formation of esters from TBIs and alcohols was instantaneous, but such reactions were not observed in this work.[69] Instead, esterification was promoted using $H_2SO_4$ or $SOCl_2$ as catalysts in EtOH or MeOH (**Scheme 4b**). For example, TBI 1b (0.78 g, 2.92 mmol) was added in a round bottom flask with excess EtOH (12 mL) with $SOCl_2$

(2.0 mL), and the mixture became fully soluble when heated at reflux. After the reaction, the crude mixture was washed with diethyl ether ($Et_2O$) and aq. $NaHCO_3$ (pH = 9). Finally, the product (compound d) was obtained via drying the organic layer (67% yield). TBI products 1b and 2b were successfully transformed into the corresponding esters reacting with EtOH and MeOH, respectively.

The $^1$H NMR spectrum for the product of TBI (1b) with EtOH in $CDCl_3$ clearly supports the diethylterephthalate (DET) formation as the product (**Figure S28**). Similarly, TBI (1b) produces DMT when reacted with MeOH (79% yield) (**Figure S29**). TBI (2b) exhibited equal reactivity to form esters (DET and DMT) with alcohols in the presence of $SOCl_2$ (**Figures S30** and **S31.)**

### 6.3 Preparation of 2,2′-(1,4-Phenylene)bis[1H-benzimidazole] using TBI

Benzimidazoles comprise a significant class of imidazole derivatives, having been found in their practical applications in pharmacology[70], dye-sensitized solar cells[71], and thermally stable poly(benzimidazole) materials.[72] Previously, Fukushima et al. reported obtaining similar compound through organocatalytic depolymerization of PET with o-PDA (8 eq.) and TBD catalyst at 190 °C after 72 h with 62% yield.[73] Herein, TBIs are shown to be able to form 2,2'-bisbenzimidazole (compound e) with *o*-PDA (2.1 eq.) via solvent assisted method after 6 h with 86% yield. To date, several synthetic approaches have been developed for this compound. Among them, the most effective method involves the acid-catalyzed condensation of *o*-PDA with TA, terephthalaldehyde, or terephthalonitrile, leading to ring closure. The current results validate the use of TBI (1b) as a suitable reagent for this purpose.

As shown in **Scheme 4c**, 13.87 mmol of *o*-PDA, 6.61 mmol of 1b, and a 60 mL mixture of PPA and $H_3PO_4$ (3:2 ratio) were taken in a 250 mL round-bottom flask under a $N_2$ atmosphere.

The initial reaction temperature was set to 70 °C and was gradually increased to 210 °C over 6 h. After this time, the reaction was allowed to cool and was poured into a chilled solution of 15 wt% aq. NaOH and a precipitate immediately formed. Additional aq. NaOH was added dropwise to achieve a solution of pH = 7, whereby a pale green solid powder was obtained and collected via vacuum filtration. The product was purified by recrystallization from abs. EtOH yielding an off-white powder, which was dried at 80 °C under vacuum. **Figure S32** (top) presents the $^1$H NMR spectrum of this compound in DMSO-$d_6$. Distinguished N-H protons at $\delta$ 13 ppm and bisbenzimidazole protons at $\delta$ 7 to 8 ppm confirm the formation of the product. In addition to the purity obtained, the FTIR spectrum revealed the absence of C=O stretching band between 1780 and 1650 cm$^{-1}$, and N-H stretching was found around 3059 cm$^{-1}$, confirming the product formation **(Figure S32 (bottom)).**

## 7. Conclusions and Outlook

This work has shown that imidazole and related compounds are effective agents for depolymerizing PET without the need for a cosolvent, forming symmetric TBI compounds. Imidazolysis adds a tool for plastic waste upcycling, and the resulting TBI compounds can be used as versatile intermediates to convert to other small molecules. These results confirm that TBIs can be converted valuable terephthalates and terephthalamides, highlighting the production of TA, DMT, and bisbenzimidazole. Notably, the methodology employed here excludes the extreme reaction conditions to recover TA and DMT, typically compared to the direct hydrolysis and methanolysis of PET, offering a moderate and potentially more sustainable alternative for material recovery from polyester waste.

Therefore, the resultant TBIs have terephthaloyl moieties which demonstrate advantageous electrophilic properties, and present opportunities for more types of reactions/products than have been explored here. We also plan to further study imidazolysis of other polyesters, PUs, and potentially polyamides, as well as the use of TBI products as monomers for forming polyesters and polyamides.

## Supporting Information

The Supporting Information is available free of charge at

https://pubs.acs.org/doi/10.1021.acsapm.XXXXXX

Imidazolysis mechanism scheme; photograph of microwave reactor; photographs of imidazolysis products; $^1$H NMR, $^{13}$C NMR, and FTIR spectra for products; solubility of TBI in common solvents; DFT analysis; HSQC and HMBC NMR.

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