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# Designing Thermally Stable Organocatalysts for Poly(ethylene terephthalate) Synthesis: Toward a One-Pot, Closed-Loop Chemical Recycling System for PET

Shu Kaiho, Ali Al Rida Hmayed, Kayla R. Delle Chiaie, Joshua C. Worch, and Andrew P. Dove*

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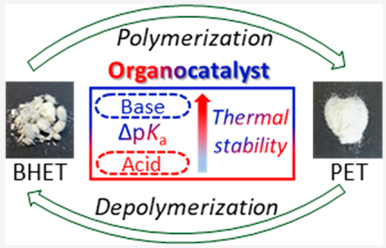
**ABSTRACT:** Organocatalysis provides robust methodology to furnish "greener" routes to polymer synthesis. However, the application toward the synthesis of aromatic polymers via step-growth polymerization is an area that justifies more investigation, as a consequence of the poor thermal stability of many organic catalysts and the high reaction temperatures commonly required. In this study, thermally stable organic salts consisting of an organic base and an organic acid were explored to understand key elements required for the bulk synthesis of poly(ethylene terephthalate) (PET) at 270 °C. The $\Delta pK_a$ values of the salts played an important role in the thermal stability such that the salts with higher $\Delta pK_a$ values showed higher stability because of the strong acid−base interactions. The 1,5,7-triazabicyclo[4.4.0]-dec-5-ene (TBD) salts with high $\Delta pK_a$ values (≥16.9) showed the best catalytic activity among the investigated salts in terms of both low amounts of side reactions and discoloration. The thermal and chemical stability of the salts also affected the polymer properties. Dimerization side reactions that lead to defects in the polymer backbone were found to occur more readily in salts containing strong acids as components, particularly as the $\Delta pK_a$ between the acid−base components decreased. The discoloration of the PET sample was also correlated to the thermal stability of the organic salt catalyst, with a lower stability generally leading to enhanced discoloration likely due to decomposition of base components. Polymerization−depolymerization cycles were also investigated with the TBD:*p*-toluenesulfonic acid (TSA) salt and the feasibility of simple, closed-loop recycling of PET with the system was established.




## INTRODUCTION

Aromatic polymers produced via step-growth polymerization such as poly(phenylene sulfide) (PPS), poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and polyamide (PA) exhibit high performance characteristics such as high thermal stability, high chemical resistance, and good mechanical strength.[1−9] Among these polymers, PET represents one of the most industrially used thermoplastics especially in the manufacture of food packaging, beverage bottles, films, and synthetic fibers.[4,10,11] However, its conventional polymerization conditions are harsh and typically require high temperatures (ca. ≥ 270 °C), high vacuum, and long reaction times, which can lead to monomer decomposition and unwanted side reactions that discolor the polymer and lower its molecular weight.[12] PET synthesis therefore requires a thermally stable catalyst, most commonly metal-based species. Industry-preferred catalysts are composed of antimony, titanium, or germanium; however, these species can be highly toxic, expensive, and/or lead to coloration of the resulting PET.[13]

Organocatalysts are considered highly attractive for application in polymer synthesis as they have the potential to reduce the environmental footprint of the polymerization process in addition to their often-lower toxicity.[14−18] However, utilizing these types of catalysts in the synthesis of aromatic polymers via step-growth polymerization has not been thoroughly investigated, most likely a consequence of the typically poor thermal stability of many organic catalysts. Recently, organic acid−base salts have been studied as thermally stable organic catalysts for ring-opening polymerization (ROP), step-growth polymerization,[19] and depolymerization.[20−22] In particular, creatinine carboxylates and imidazole-, *N*,*N*-dimethyl-4-aminopyridine (DMAP)-, and benzoic acid (BA)-based salts were used in the synthesis of aliphatic polyesters for the ROP of lactides.[23−30] Thiourea-based salts were also applied in aliphatic polyester amide synthesis,[31] and the 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene:trifluoroacetic acid (MTBD:TFA) salt was investigated in the synthesis of aliphatic polycarbonates,[32] again by ROP. However, these organic acid−base salts have been used only in ROP under relatively low temperatures (up to 170 °C). More recently, the 1,5,7-triazabicyclo[4.4.0]dec-5-ene:methanesulfonic acid (TBD:MSA) salt has been shown to have

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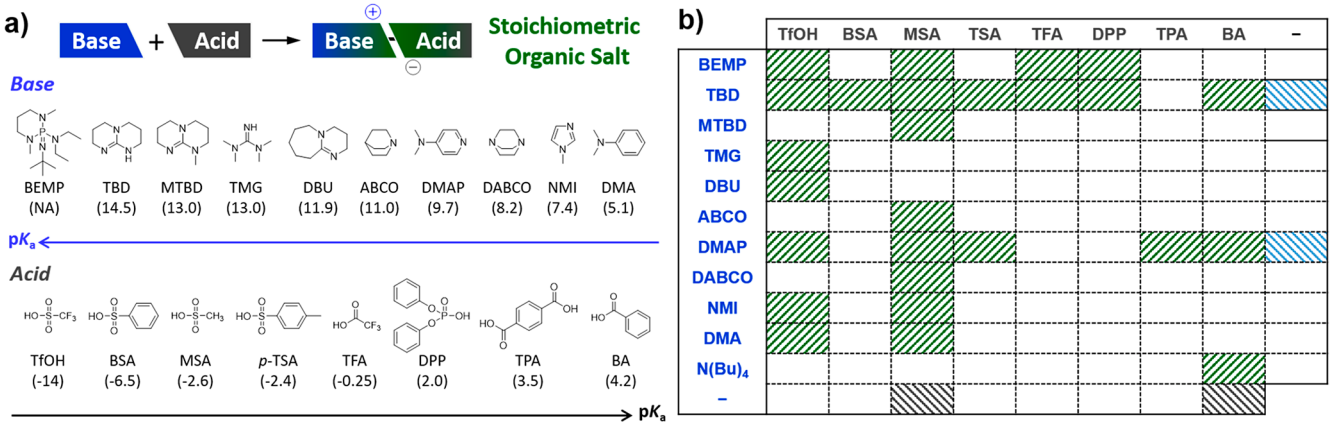


**Figure 1.** (a) Chemical structures of all the bases and acids employed with their p$K_a$ values under aqueous conditions (see the Supporting Information). (b) Summary of screened acid−base combinations indicated by shaded boxes: green = organic salt, blue = base only, and gray = acid only.

extremely high thermal stability on account of the formation of an ionic pair between the protonated cation $[TBDH]^+$ and the $[MSA]^-$ anion, in addition to the hydrogen bond between the N−H moiety of TBD and one of the oxygen atoms of the MSA sulfonyl group.[20] After being first studied as a catalyst for bulk ROP of ε-caprolactone under mild conditions,[33] recently, it has been investigated for the preparation of aliphatic polyethers[34,35] and PET[20,36] via step-growth polymerization at 200−250 °C. Subsequently, the organic salt DBU-BA (1,8-diazabicyclo[5.4.0]undec-7-ene/benzoic acid) was used as a catalyst for the bulk step-growth polymerization of PET from dimethyl terephthalate and ethylene glycol and from bis(2-hydroxyethyl) terephthalate (BHET).[36] However, despite the wide range of available acids and bases, reports of utilizing these catalyst species in step-growth polymerization remain limited, and the development of a structure−function understanding has not been possible.

Herein we report our studies to understand the structural elements that are critical to the application of organic salts as catalysts in the step-growth polymerization of PET under reaction conditions relevant to industry (i.e., 270 °C under vacuum). Acid−base organic salts are investigated to understand the differences in their thermal stability and catalytic activity including the amounts of side reaction and discoloration. We also demonstrate the feasibility of closed-loop polymerization−depolymerization cycles of PET using a highly stable TBD:*p*-toluenesulfonic acid (TSA) salt.

## ■ RESULTS AND DISCUSSION

Initially, we prepared a library of stoichiometric organic salts that consist of a nitrogen-based organic base and an organic acid via straightforward neutralization reactions in an organic solvent (Figure 1). The bases and acids were selected to cover a wide range of p$K_a$ values (p$K_a$ = −14 to 4.2 for acids; p$K_a$H = 4.1 to 14.5 for bases) to increase the surveyed chemical space beyond typical strong acid/strong base pairings such as TBD:MSA.[20] The formation of the salts was confirmed by diagnostic changes in their $^1$H NMR spectra before and after mixing. For example, the spectra of the series of salts prepared with TBD revealed the loss of both the N−H proton signal of TBD at $\delta$ = 4−5 ppm and the O−H proton signal of various acids significantly further downfield to reveal a broad N−H proton resonance from $\delta$ = 7.39−10.93 ppm that integrates to two protons in intensity. In general, the downfield shift of N−H proton signal in salts can be correlated to the acid strength.

To operate as polymerization catalysts for PET synthesis at high temperature (i.e., 270 °C), the thermal stability of the salts is a key parameter. As such, thermogravimetric analyses (TGA) were conducted for each organic salt, both as a function of temperature and under isothermal heating conditions at 270 °C for 5 h (Figures 2, S3−S10, S12, and

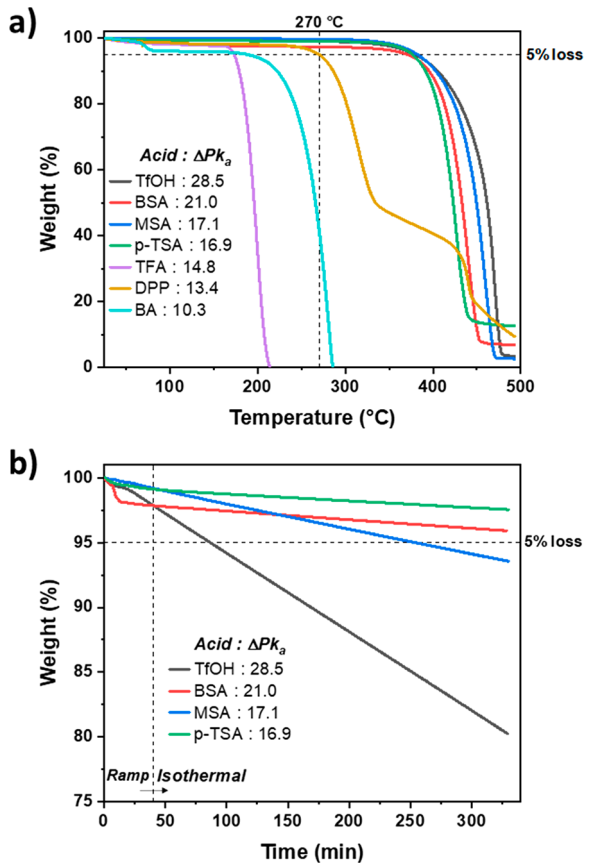


**Figure 2.** TGA thermograms for various TBD-based salts: (a) dynamic heating at a rate of 10 °C min$^{-1}$; (b) isothermal heating at 270 °C for 5 h after initial temperature ramp from 25 to 270 °C at 10 °C min$^{-1}$. Separation of heating phases indicated by the vertical hashed line.


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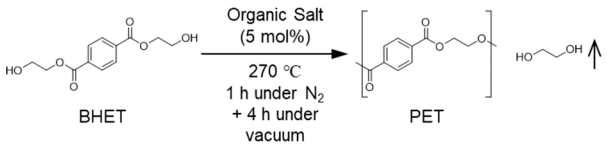
S13). The dynamic heating experiments revealed that salts with higher $\Delta pK_a$ values, as assessed by the differences between acid and base components,[37−41] generally exhibited higher thermal stability, i.e., higher 5 wt % loss temperatures (Figure 2a). These data indicate that the TBD salts with $\Delta pK_a$ values of 15 or higher showed high thermal stability, and many derivatives were stable up to temperatures of at least 270 °C, which is required for synthesis of PET. Interestingly, further examination of the most stable salts by isothermal TGA at 270 °C revealed that those salts with $\Delta pK_a$ values closer to 15 were the most stable over 4 h (Figure 2b). We postulate that the correlation between thermal stability and $\Delta pK_a$ is a consequence of the strong interactions between the acid and base (Figure S11). However, this relationship between $\Delta pK_a$ and thermal stability is not perfectly consistent with the data; i.e., the salts with the greatest $\Delta pK_a$ are not the most thermally stable. For example, TBD:MSA is more thermally stable than either TBD:BSA or TBD:TfOH while $\Delta pK_a$ for the former is lower (Figure 2b). This could be related to free (unbound) acid or base arising during heating or possibly due to decomposition of the salt species itself. As such, the stability of the constituent base or acid alone should also be considered, and this value may not necessarily correlate to the respective $pK_a$ values (Figures S1 and S2). Notably, initial exploration of the phosphazene base, 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), salts was less stable than this relationship would predict; however, this instability might be from the steric hindrance around the protonated nitrogen atom (Figures S12 and S13).

While it is clear that the $\Delta pK_a$ has an important role in determining the thermal stability of the resulting organic salt, we were also interested to understand how this parameter influenced the catalyzed step-growth polymerization of BHET to produce PET because BHET is a commonly encountered monomer for closed-loop chemical recycling of PET (Scheme 1). The polymerization was conducted at 270 °C with stirring

**Scheme 1. Polymerization of BHET Using a Salt Catalyst**




for 1 h under a nitrogen atmosphere to avoid unwanted oxidation as oligomers formed.[42] Then, at the same temperature, vacuum was applied for 4 h to eliminate the ethylene glycol byproduct, which further increased monomer/oligomer conversion and the overall polymer molecular weight.[43]

The resulting polymers were analyzed by $^1$H NMR spectroscopy to determine molecular weight by end-group analysis and assess the presence of diethylene glycol (DEG) defects in the polyester backbone that can result from BHET dimerization. Beyond the presence of ether linkages, no additional in-chain defects were detected in the synthesized PET samples. However, DEG defects within PET can cause a decrease in the glass transition temperature, melting temperature, and crystallinity of the sample which subsequently impacts hydrolytic and thermo-oxidative stability.[44] Therefore, it is desirable to identify catalysts that do not promote the formation of ether linkages within the polymer. Notably, the spectra were collected within 2 h after dissolving the PET because esterification reactions between the hydroxyl end groups in PET and trifluoroacetic acid (added to increase polymer solubility[45]) have been reported at ambient temperature.[46]

All acid−base combinations, except for the combinations of TBD:weak acids, led to high number-average molecular weight ($M_n$ > 15 kg mol$^{-1}$) PET polymers, which are comparable to typical commercial PET samples (Figure S14 and Table S1).[47] However, the relationship between $M_n$ and $\Delta pK_a$ reveals no clear trend. Notably, insoluble black solids were obtained for reactions that employed TBD salts featuring weak acids. This is consistent with observations for PET produced using just TBD and hence may be explained by the presence of unbound TBD from the less-stable salts.[36] Conversely, all TBD salts generally led to low levels of DEG incorporation into the isolated PET (Figure S15). A clearer relationship was observed between the level of DEG unit formation and $\Delta pK_a$ (Figure 3). The salts

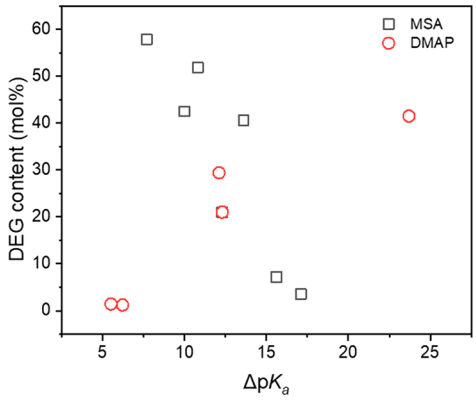



**Figure 3.** Amount of diethylene glycol units as a function of $\Delta pK_a$ values for various organic salts of either MSA/base or DMAP/acid.

containing MSA, which is a strong acid with a low $pK_a$ value, led to higher levels of dimerization as $\Delta pK_a$ decreased (Figure 3). Organic salts exist in equilibria of a conjugate pair, and the individual acid and base. As a function of energetic barrier, the salts with lower $\Delta pK_a$ values are more likely to exist in equilibrium such that low levels of strong free acid could be present in the system and catalyze dimerization.

To gain a deeper understanding of this observation, a wider range of acid:base salts were applied in the synthesis of PET from BHET at 270 °C. Specifically, BA and DMAP was investigated as a weak acid/base combination to provide a low $\Delta pK_a$ value salt with a weak acid conjugate. The DMAP:BA salt led to low dimerization (1.4 mol %). Investigation of a wider range of DMAP-based salts revealed that those with higher $\Delta pK_a$ values led to higher dimerization despite higher $\Delta pK_a$ values (Figure 3). This supports the hypothesis that a small amount of strong acid, existing in equilibria, likely promotes dimerization reactions. As such, it can be concluded that the use of the most stable salts which do not release strong acids, or the use of weak acids, is important to inhibit the ether-forming side reaction.

The relationships between polymerization reaction times and $M_n$ and polymerization reaction times and degrees of dimerization have also been investigated to understand how the reactions proceed. The TBD:MSA salt and the TBD:TfOH salt were employed in the polymerization experiments, and it was revealed that when the polymerization is conducted under $N_2$ flow, an increase in DEG units within the polymer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backbone is only observed during the first hour of reaction time. As may be expected, when the polymerization is subsequently placed under vacuum, the most significant increases in polymer $M_n$ occur (see Figure S15). These observations are consistent with EG buildup from oligomer formation before pressure reduction to achieve higher molecular weight polymers. Upon removal of the EG under vacuum, the likelihood of dimer formation is reduced. This is consistent with the reported kinetic studies of diethylene glycol formation in the preparation of PET.[48−51]

As a final aspect of the study, we investigated how the catalysts studied influenced the color of the final polymers. Polymer colors were quantified with the International Commission on Illumination (CIE) $L^*a^*b^*$ color space system[52] by calculation using UV−vis spectra of polymer solutions, in which $L^*$ indicates the lightness of the sample ($L^*$ = 100, white; $L^*$ = 0, black), $a^*$ represents the red-green axis (positive, red; negative, green), and $b^*$ represents the yellow-blue axis (positive, yellow; negative, blue). No obvious trends with $L^*$ and $a^*$ values were observed because of the low concentrations of the polymer solutions and the type of the colors (yellow-brown), respectively. However, a weak correlation between the salt stability and $b^*$ values was observed such that less thermally stable salts, as determined in distinct TGA experiments, produced PET samples with higher $b^*$ values, indicative of yellow discoloration (Figure 4). In addition to this trend, the polymer color was whitish ($b^*$ = 0.3) when only MSA was employed as a catalyst. This indicates that the origin of the discoloration may be a result of base decomposition. Salts with 0 wt % remaining percentages of catalyst were so unstable that an acid and a base may have been volatilized and did not significantly affect polymer colors. It was assumed that the use of stable salts is important to inhibit the discoloration.

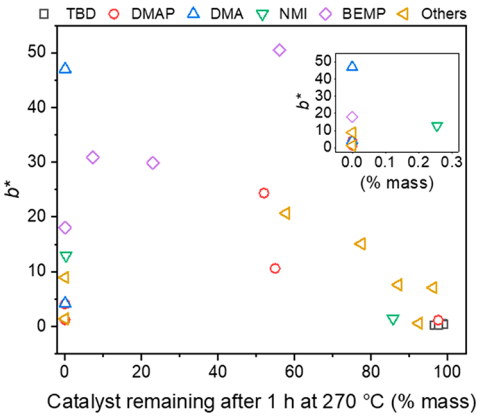


**Figure 4.** Colorimetric $b^*$ values for synthesized PET as a function of catalyst thermal stability. Inset highlights PET color using catalysts that fully decomposed. The remaining percentage of the catalyst was determined in separate TGA experiments (isothermal heating of catalysts at 270 °C).

While organic catalysts can typically be readily removed from polymer products by washing, it adds a process step to the polymer synthesis, and as such, on large scales, catalysts are typically left in polymers after the reaction is complete. Given the high thermal stability of the TBD:*p*-toluenesulfonic acid (TSA) catalyst (2.5% weight loss for 5 h at 270 °C) and the previous application of comparable organic salt catalysts for depolymerization of PET, we postulated that catalyst remaining after the PET synthesis could be reactivated for depolymerization. To this end, following polymerization of BHET with 5 mol % TBD:*p*-TSA salt, the resultant polymer was depolymerized at 180 °C by the addition of EG (20 equiv), without any purification or catalyst addition (Figure 5). The depolymerization temperature was fixed at 180 °C because this is near the boiling point of EG, and previous studies have shown a dramatic decrease in reaction rates at lower temperatures.[53,54] The PET was fully depolymerized (100% conversion) in 24.5 h, as indicated by the reaction mixture becoming homogeneous since the PET sample is insoluble. No remaining PET was recovered after filtration of the reaction mixture. The depolymerization reaction yielded 56.7% of isolated BHET, most likely below conversion because of poor recovery through precipitation with added water. The depolymerization reaction rate was comparable to the reaction of PET flakes with TBD:MSA salt addition as reported previously (BHET yield was 27% after 12 h reaction with 12 mol % of TBD:MSA salt and 20 equiv of EG at 180 °C).[20] This means that the catalyst inside the polymer mixture was active under the depolymerization reaction conditions even after the harsh polymerization reaction. The feasibility of simple closed-loop recycling of PET with this organocatalysis system was thus demonstrated.

## ■ CONCLUSION

A series of organic acid−base salts were synthesized to act as catalysts in the polymerization of BHET to PET at 270 °C under reduced pressure. The $\Delta pK_a$ value between acid and base components of the salt was found to play an important role in the thermal stability such that the salts with higher

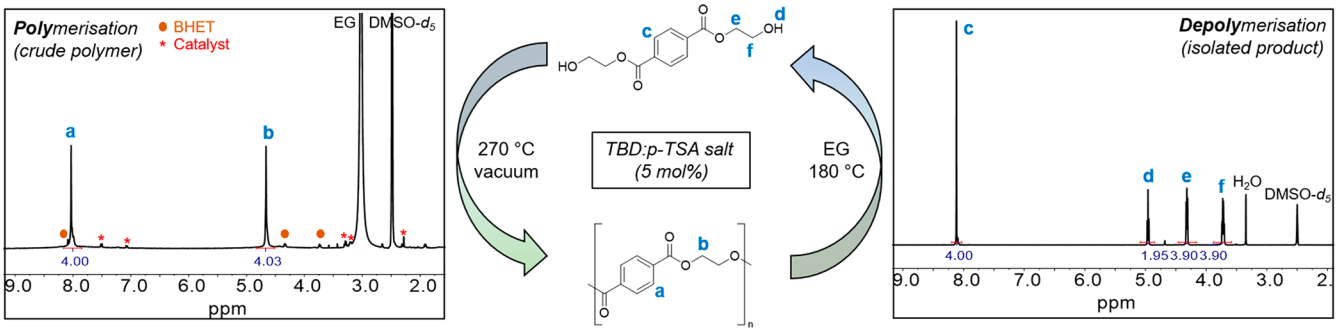


**Figure 5.** Simple closed-loop recycling of PET with the organocatalysis system, with $^1$H NMR spectra of the PET and the BHET produced within the polymerization/depolymerization cycle (400 MHz, 398 K, DMSO-$d_6$).


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$\Delta pK_a$ values displayed a higher stability, most likely as a consequence of the stronger acid−base interactions. All of the investigated acid−base salts, with the exception of TBD:weak acid salts, were active for BHET polymerization and led to high $M_n$ (≥15 kg mol$^{-1}$) PET polymers. The results indicated that the properties of the produced PET were significantly influenced by the thermal stability of the salts. Ether linkages in the PET were formed by a dimerization side reaction taking place as a result of dissociated strong acid, with polymer discoloration resulting from dissociated bases. It was revealed that the use of stable salts is important, and the combinations of strong acids and strong bases as exemplified by TBD salts with high $\Delta pK_a$ values (≥16.9) were the best among the investigated salts in terms of both the side reaction and the discoloration. A polymerization−depolymerization cycle was also investigated with the most stable TBD:*p*-TSA salt and showed that organic salts left in the polymer after polymerization could be applied to depolymerize the PET back to BHET at 180 °C without any purification or catalyst addition, only the addition of EG. The feasibility of simple closed-loop recycling of PET with this organocatalysis system was demonstrated.

## ■ EXPERIMENTAL SECTION

**Materials.** 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, ≥98%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, ≥98%), 1,1,3,3-tetramethylguanidine (TMG, ≥99%), 4-(dimethylamino)pyridine (DMAP, ≥98%), 1,4-diazabicyclo[2.2.2]octane (DABCO, ≥99%), 1-methylimidazole (NMI, ≥99%), *N*,*N*-dimethylaniline (DMA, ≥99%), trifluoromethanesulfonic acid (TfOH, ≥98%), benzenesulfonic acid (BSA, ≥98%), methanesulfonic acid (MSA, ≥99%), terephthalic acid (TPA, ≥98%), benzoic acid (BA, ≥99.5%), tetrabutylammonium benzoate ($Bu_4N$:BA, ≥99%), and bis(2-hydroxyethyl) terephthalate (BHET, ≥94.5%) were purchased from Sigma-Aldrich. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, ≥99%), quinuclidine (ABCO, ≥97%), *p*-toluenesulfonic acid monohydrate (*p*-TSA monohydrate, ≥98%), trifluoroacetic acid (TFA, ≥99%), and diphenyl phosphate (DPP, ≥97%) were purchased from Alfa Aesar. 2-*tert*-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP, ≥98%) and ethylene glycol (EG, ≥98.5%) were purchased from ACROS Organics. All chemicals except for DBU were used without further purification. DBU was purified by distillation under vacuum using a Kugelrohr (80 °C, $10^{-2}$ mbar). Acetone, chloroform, ethanol, diethyl ether, dichloromethane, tetrahydrofuran (THF), and *N*-methyl-2-pyrrolidone (NMP) were of ACS grade or higher. NMP was purified by distillation under vacuum using a Schlenk line.

**Instrumentation.** NMR $^1$H (400 MHz), $^{13}$C (101 MHz), $^{19}$F (376 MHz), and $^{31}$P (162 MHz) spectra were recorded on a Bruker spectrometer. The $^{31}$P NMR spectra were referenced to an external standard (85% $H_3PO_4$). The $^{19}$F NMR spectra were referenced to an external standard ($CF_3COOH$). Organic salts were dissolved in DMSO-$d_6$ or $CDCl_3$, and chemical shifts were referenced to DMSO-$d_6$ (2.5 ppm in $^1$H NMR and 39.9 ppm in $^{13}$C NMR) or $CDCl_3$ (7.26 ppm in $^1$H NMR and 77.0 ppm in $^{13}$C NMR). Polymers were dissolved either in a mixture of $CDCl_3$ and trifluoroacetic acid (TFA) (8:1, v/v), with chemical shifts referenced to $CDCl_3$, or in DMSO-$d_6$ at 100 °C. The spectra of polymers were collected within 2 h after dissolving the polymer. Thermogravimetric analysis (TGA) was performed by a TA Instruments TGA Q550 under a nitrogen atmosphere. Weight loss as a function of temperature was examined under the programmed heating condition from room temperature to 500 °C at a rate of 10 °C min$^{-1}$. Weight loss as a function of time was examined under the programmed heating condition from room temperature to 270 °C at a rate of 10 °C min$^{-1}$ followed by the isothermal heating condition at 270 °C for 5 h. Mass spectrometry was performed on a Waters Xevo G2-XS, a Waters LCT, or a Waters SQD 2. FT-IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer using the ATR technique. Spectra were recorded between 4000 and 650 cm$^{-1}$, and all spectra were averaged over 32 scans. Elemental analysis in the presence of oxygen was performed with a CE Instruments EA1110 elemental analyzer following in vacuo drying to remove any solvent or water impurities. UV−vis spectroscopy was performed on Evolution 350 UV−vis spectrophotometer equipped with a xenon flash lamp light source and a dual matched silicon photodiodes detector. Quartz cells (170−2000 nm) from Hellma with two polished sides were used for examining the absorption spectral data by using Thermo INSIGHT-2 v.10.0.30319.1 software. Colorimetry analyses were performed using an Evolution 350 UV−vis spectrophotometer. All samples were prepared at concentrations of 5 mg mL$^{-1}$ using a mixture solvent of chloroform:trifluoroacetic acid (8:1).

**Molecular Weights and Diethylene Glycol (DEG) Content Determination.** Number-average molecular weights and amounts of DEG unit were analyzed by $^1$H NMR spectroscopy based on the ratios of protons of the oxyethylene unit ($\delta$ = 4.77 ppm) to the hydroxyethyl ($\delta$ = 4.17 ppm), and protons of the oxyethylene unit to the oxidiethylene methylenes ($\delta$ = 4.08 ppm) in a $CDCl_3$/TFA (8/1) mixture.[44]

**Colorimetry Analysis.** The International Commission on Illumination (CIE) $L^*a^*b^*$ color space system was used to evaluate the color of the synthesized polymers. $L^*$ indicates the lightness of the sample ($L^*$ = 100, white; $L^*$ = 0, black). $a^*$ represents the red-green axis (positive values indicate red, negative values indicate green). $b^*$ represents the yellow-blue axis (positive values indicate yellow, negative values indicate blue). Values were calculated under the condition of a standard illuminant D65 light source at 2°, using the following equations. $X_n$, $Y_n$, and $Z_n$ values in Table T3, $S(\lambda)$ values in Table T1, and $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ values in Table T4 were used for the calculation as outlined below:[52]

$$L^* = 116f(Y/Y_n) - 16$$

$$a^* = 500[f(X/X_n) - f(Y/Y_n)]$$

$$b^* = 200[f(Y/Y_n) - f(Z/Z_n)]$$

where

$$f(X/X_n) = (X/X_n)^{1/3} \text{ if } (X/X_n) > (24/116)^3$$

$$f(X/X_n) = (841/108)(X/X_n) + 16/116$$

$$\text{if } (X/X_n) \leq (24/116)^3$$

and

$$f(Y/Y_n) = (Y/Y_n)^{1/3} \text{ if } (Y/Y_n) > (24/116)^3$$

$$f(Y/Y_n) = (841/108)(Y/Y_n) + 16/116$$

$$\text{if } (Y/Y_n) \leq (24/116)^3$$

and

$$f(Z/Z_n) = (Z/Z_n)^{1/3} \text{ if } (Z/Z_n) > (24/116)^3$$

$$f(Z/Z_n) = (841/108)(Z/Z_n) + 16/116 \text{ if } (Z/Z_n) \leq (24/116)^3$$

$$X = K\sum_{380}^{780} S(\lambda)\bar{x}(\lambda)T(\lambda)\Delta\lambda$$

$$Y = K\sum_{380}^{780} S(\lambda)\bar{y}(\lambda)T(\lambda)\Delta\lambda$$

$$Z = K\sum_{380}^{780} S(\lambda)\bar{z}(\lambda)T(\lambda)\Delta\lambda$$


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$$K = 100/\sum_{380}^{780} S(\lambda)\bar{y}(\lambda)\Delta\lambda$$

where $X$, $Y$, and $Z$ are tristimulus values. $X_n$, $Y_n$, and $Z_n$ are tristimulus values of a specified white color stimulus. $K$ is the normalizing constant. $S(\lambda)$ is the relative spectral power distribution of the illuminant at wavelength $\lambda$, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ are color-matching function values of a standard colorimetric observed at wavelength $\lambda$. $T(\lambda)$ is the spectral transmittance wavelength $\lambda$ ($T(\lambda)$ was employed instead of spectral reflectance $R(\lambda)$ which is normally used, in this case of solution measurement), and $\Delta\lambda$ is the wavelength interval for calculation (5 nm in this case).

**Synthesis and Characterization of Organic Salts.** *TBD:TfOH (1:1) Salt.* Acetone (5 mL), TBD (0.696 g, 5 mmol), and TfOH (0.750 g, 0.442 mL, 5 mmol) were mixed in a Schlenk flask. The mixture was cooled in the refrigerator, but solids were not formed. The solution was precipitated in diethyl ether (50 mL), and the subsequent solids were collected. The solids were dissolved in acetone (2 mL) and heated in a Schlenk flask at 65 °C under $N_2$ for 30 min. The mixture was cooled in the refrigerator, but solids were not formed. The solid was precipitated in diethyl ether (30 mL), filtered, washed with diethyl ether, and dried under vacuum at room temperature overnight (0.576 g, 40%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.39 (br s, 2H, N*H*), 3.28 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2NH$), 3.18 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $NCH_2CH_2$), 1.87 (quin, 4H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 150.54 (NC(N)N), 120.68 (quin, $CF_3$), 46.27 ($CH_2CH_2N$), 37.61 ($CH_2CH_2NH$), 20.25 ($CH_2CH_2CH_2$). MS (ESI): $m/z$ 140.13 ($TBDH^+$), 148.97 ($TfO^-$). FT-IR (ATR): max/cm$^{-1}$ 3304, 3234, 3163 (NH, OH), 3040 and 2984 ($CH_2$), 2880 ($N^+$−H), 1624 (C═N), 1524 (NH), 1446, 1382, 1356, 1319, 1274, 1222, 1147, 1061, and 1021 ($SO_2$, $CF_3$). Anal. Calcd for $C_8H_{14}F_3N_3O_3S$: C 33.2; H 4.9; N 14.5; S 11.1%. Found: C 33.4; H 4.7; N 14.5; S 11.3%.

*TBD:BSA (1:1) Salt.* Acetone (20 mL), TBD (0.696 g, 5 mmol), and BSA (0.791 g, 5 mmol) were mixed and heated at 65−70 °C under $N_2$ for 1 h, but the resultant solid was not soluble. The mixture was then cooled in the refrigerator, and the solid was collected. The solid was further treated by adding acetone (100 mL) and heating in a round-bottom flask at 65−70 °C under $N_2$ for 1 h to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. Crystals were collected, washed with acetone, and dried under vacuum at room temperature overnight (0.803 g, 54%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.61 (m, 2H, SCC*H*), 7.49 (br s, 2H, N*H*), 7.33 (m, 3H, CCHC*HCH*), 3.26 (t, 4H, $^3J_{H-H}$ = 6.0 Hz, $CH_2CH_2NH$), 3.17 (m, 4H, $NCH_2CH_2$), 1.86 (quin, 4H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 150.54 (NC(N)N), 148.10 (SCCH), 128.51 (CCHCHCH), 127.68 (CCHCHCH), 125.44 (CCHCHCH), 46.23 ($NCH_2CH_2$), 37.57 ($CH_2CH_2NH$), 20.24 ($CH_2CH_2CH_2$). MS (ESI): $m/z$ 140.13 ($TBDH^+$), 157.10 ($BSA^-$). FT-IR (ATR): max/cm$^{-1}$ 3275, 3211, and 3159 (NH, OH), 3051 and 2977 ($CH_2$), 2872 ($N^+$−H), 1628 (C═N), 1535 (C═C), 1472, 1438, 1364, 1319, 1293, 1207, 1170, 1170, 1118, 1062, and 1025 ($SO_2$). Anal. Calcd for $C_{13}H_{19}N_3O_3S$: C 52.5; H 6.4; N 14.1%. Found: C 52.5; H 6.7; N 14.0%.

*TBD:MSA (1:1) Salt.* TBD:MSA (1:1) salt was synthesized as reported previously.[20] Acetone (90 mL), TBD (2.00 g, 14.3 mmol), and MSA (1.38 g, 0.932 mL, 14.3 mmol) were mixed in a Schlenk flask at 65−70 °C under $N_2$. The mixture was heated for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. Crystals were collected and washed with acetone. The crystals were further treated by adding acetone (80 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. Crystals were collected, washed with acetone, and dried under vacuum at room temperature overnight (1.86 g, 55%). Characterization is consistent with that reported previously.[20] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.58 (s, 2H, N*H*), 3.27 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $NHCH_2CH_2$), 3.17 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $NCH_2CH_2$), 2.34 (s, 3H, $CH_3$), 1.87 (quin, 4H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 150.58 (NC(N)N), 46.23 ($CH_2CH_2N$), 39.74 ($CH_3$), 37.52 ($CH_2CH_2NH$), 20.26 ($CH_2CH_2CH_2$).

*TBD:p-TSA (1:1) Salt.* TBD (0.696 g, 5 mmol) was dissolved in acetone (15 mL). *p*-TSA monohydrate (0.951 g, 5 mmol) was dissolved in acetone (5 mL). These solutions were mixed and heated at 65−70 °C under $N_2$ for 30 min in a Schlenk flask. The mixture was cooled in the refrigerator but solids were not formed. Solids were precipitated in diethyl ether (60 mL), filtered, and dried under vacuum at room temperature overnight. The solid was further treated by adding acetone (10 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. Crystals were collected and dried under vacuum at room temperature overnight (0.830 g, 53%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.51−7.49 (m, 4H, $^3J_{H-H}$ = 7.9 Hz, SCC*H*CH, N*H*), 7.13 (m, 2H, $^3J_{H-H}$ = 7.9 Hz, CHC*H*$CCH_3$), 3.26 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2NH$), 3.17 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $NCH_2CH_2$), 2.29 (s, 3H, $CH_3$), 1.86 (quin., 4H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 150.55 (NC(N)N), 145.40 ($CHCCH_3$), 137.82 (SCCH), 128.13 ($CHCHCCH_3$), 125.48 (SCCHCH), 46.23 ($NCH_2CH_2$), 37.57 ($CH_2CH_2NH$), 20.78 ($CH_2CH_2CH_2$), 20.24 ($CH_3$). MS (ESI): $m/z$ 140.20 ($TBDH^+$), 171.07 ($p$-$TSA^-$). FT-IR (ATR): max/cm$^{-1}$ 3275, 3211, and 3156 (NH, OH), 3051, 3010, 2973, 2951, and 2947 ($CH_2$), 2865 ($N^+$−H), 1628 (C═N), 1539 and 1490 (C═C), 1438 1393, 1360, 1319, 1218, 1151, and 1114 ($SO_2$). Anal. Calcd for $C_{14}H_{21}N_3O_3S$: C 54.0; H 6.8; N 13.5; S 10.3%. Found: C 54.0; H 6.6; N 13.7; S 10.1%.

*TBD:TFA (1:1) Salt.* TBD:TFA (1:1) salt was synthesized as reported previously.[55−57] TBD (0.696 g, 5 mmol) was dissolved in acetone (15 mL). TFA (0.570 g, 0.383 mL, 5 mmol) was added. The mixture was mixed and heated at 65−70 °C under $N_2$ for 30 min in a Schlenk flask. The mixture was cooled in the refrigerator, but a solid was not formed. The solid was precipitated in diethyl ether (50 mL) and collected. The solid was dissolved in acetone (5 mL) and heated in a Schlenk flask at 50 °C under $N_2$ for 30 min. The solid was precipitated in diethyl ether (20 mL), filtered, and dried under vacuum at room temperature overnight (0.410 g, 32%). Characterization is consistent with that reported previously.[55−57] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.99 (br s, 2H, N*H*), 3.27 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2NH$), 3.18 (t, 4H, $^3J_{H-H}$ = 5.9 Hz, $NCH_2CH_2$), 1.87 (quin, 4H, $^3J_{H-H}$ = 7.9 Hz, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 159.02 (m, $CF_3CO_2$), 150.79 (NC(N)N), 117.06 (q, $CF_3$), 46.21 ($NCH_2CH_2$), 37.47 ($CH_2CH_2NH$), 20.29 ($CH_2CH_2CH_2$).

*TBD:DPP (1:1) Salt.* Acetone (10 mL), TBD (0.696 g, 5 mmol), and DPP (1.25 g, 5 mmol) were mixed and heated at 65−70 °C under $N_2$ for 30 min in a Schlenk flask to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator, and the crystals were collected. The crystals were further treated by adding acetone (7 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. These crystals were collected and dried under vacuum at room temperature overnight (1.18 g, 60%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 8.12 (s, 2H, N*H*), 7.24 (t, 4H, $^3J_{H-H}$ = 7.4 Hz, CCHC*H*CH), 7.13 (d, 4H, $^3J_{H-H}$ = 7.4 Hz, CC*H*CH), 6.99 (t, 2H, $^3J_{H-H}$ = 7.4 Hz, CCHCHC*H*), 3.24 (t, 4H, $^3J_{H-H}$ = 6.0 Hz, $CH_2CH_2NH$), 3.12 (m, 4H, $NCH_2CH_2$), 1.84 (quin, 4H, $^3J_{H-H}$ = 5.4 Hz, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 153.49 (d, NC(N)N), 150.59 ($CH_2C(O)CH_2$), 128.93 (CCHCHCH), 122.16 (CCHCHCH), 119.81 (d, OCCHCH), 46.19 ($CH_2CH_2N$), 37.45 ($CH_2CH_2NH$), 20.26 ($CH_2CH_2CH_2$). MS (ESI): $m/z$ 140.20 ($TBDH^+$), 249.14 ($DPP^-$). FT-IR (ATR): max/cm$^{-1}$ 3271, 3197, 3125 (NH, OH), 3051 (CH), 2966 and 2936 ($CH_2$), 2858 ($N^+$−H), 1636 (C═N), 1583 and 1550 (C═C), 1487, 1438, 1397, and 1364 ($CH_2$), 1319 and 1297 (P═O), 1229, 1203, and 1196 (PO−Aryl). Anal. Calcd for $C_{19}H_{24}N_3O_4P$: C 58.6; H 6.2; N 10.8%. Found: C 58.7; H 6.2; N 10.9%.

*TBD:BA (1:1) Salt.* TBD:BA (1:1) salt was synthesized as reported previously.[58] Acetone (7 mL), TBD (0.696 g, 5 mmol), and BA (BA) (0.611 g, 5 mmol) were mixed and heated at 65−70 °C under $N_2$ for


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30 min in a Schlenk flask to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator, and the crystals were collected. The crystals were further treated by adding acetone (3 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was cooled in the refrigerator, but only a small amount of crystals was formed. The solution was precipitated in diethyl ether (30 mL), and the subsequent solids were filtered, washed with diethyl ether, and dried under vacuum at room temperature overnight (0.475 g, 36%). Characterization is consistent with that reported previously.[51] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 10.93 (s, 2H, N*H*), 7.87 (dd, 2H, $^3J_{H-H}$ = 8.2 Hz CC*H*CH), 7.38−7.28 (m, 3H, CCHC*H*C*H*), 3.26 (t, 4H, $^3J_{H-H}$ = 5.8 Hz, $CH_2CH_2NH$), 3.20 (t, 4H, $^3J_{H-H}$ = 5.8 Hz, $NCH_2CH_2$), 1.89 (quin., 4H, $^3J_{H-H}$ = 5.8 Hz, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 171.41 (COOH), 151.42 (NC(N)N), 138.78 (CCHCHCH), 129.38 (CCOOH), 128.95 (CCHCH), 127.34 (CCHCH), 46.08 ($NCH_2CH_2$), 37.16 ($CH_2CH_2NH$), 20.54 ($CH_2CH_2CH_2$).

*MTBD:MSA (1:1) Salt.* MTBD (0.766 g, 0.718 mL, 5 mmol), MSA (0.481 g, 0.324 mL, 5 mmol), and acetone (7 mL) were mixed in a Schlenk flask. A white solid was formed. Acetone (23 mL) was added, and the mixture was heated at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator, and the crystals were collected. The crystals were further treated by adding acetone (20 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized again in the refrigerator. Crystals were collected and dried under vacuum at room temperature overnight (0.622 g, 50%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.69 (s, 1H, N*H*), 3.27 (m, 8H, $CH_2NCH_2$, $CH_2CH_2NCH_3$, $CH_2CH_2NH$), 2.92 (s, 3H, $NH_3$), 2.31 (s, 3H, $SCH_3$), 1.89 (m, 4H, $CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 150.72 ($NHC(N)NCH_3$), 47.54 ($CH_2CH_2NCH_3$), 47.02 ($NCH_2CH_2$), 46.53 ($NCH_2CH_2$), 39.73 ($SCH_3$), 38.38 ($CH_2CH_2NH$), 37.02 ($NCH_3$), 20.40 ($CH_2CH_2CH_2$), 20.24 ($CH_2CH_2CH_2$). MS (ESI): $m/z$ 154.17 ($MTBDH^+$), 95.02 ($MSA^-$). FT-IR (ATR): max/cm$^{-1}$ 3219, 3170 (NH, OH), 3081, 2988, and 2939 ($CH_3$, $CH_2$), 2876 ($N^+$−H), 1591 (C═N), 1501, 1464, 1441, 1408, 1371, 1323, 1267, 1207, 1155, and 1106 ($SO_2$). Anal. Calcd for $C_9H_{19}N_3O_3S$: C 43.4; H 7.7; N 16.85; S 12.9%. Found: C 43.4; H 8.0; N 16.95; S 13.0%.

*TMG:TfOH (1:1) Salt.* TMG:TfOH (1:1) salt was synthesized as reported previously.[59−61] Diethyl ether (6 mL) was added to a Schlenk flask. TfOH (0.750 g, 0.442 mL, 5 mmol) was added dropwise to diethyl ether in an ice bath under $N_2$ flow. TMG (0.576 g, 0.627 mL, 5 mmol) was added dropwise with stirring in the same ice bath forming a two-layer solution. The lower layer was collected and dried under vacuum at room temperature overnight and then at 45 °C for 3 h (1.12 g, 84%). Characterization is consistent with that reported previously.[59−61] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.72 (br s, 2H, $NH_2$), 2.88 (s, 12H, $CH_3$). $^{13}$C: $\delta$ (ppm) 161.06 (NC(N)N), 120.68 (q, $CF_3$), 39.34 ($CH_3$).

*DBU:TfOH (1:1) Salt.* DBU:TfOH (1:1) salt was synthesized as reported previously.[62] TfOH (0.470 mL, 5.3 mmol) was added to a Schlenk flask under $N_2$ flow in an ice bath. Distilled DBU (0.767 mL, 5.1 mmol) was added into TfOH. The mixture was dried under vacuum with stirring at room temperature overnight and then at 80 °C for 24 h. The yield could not be calculated reliably due to the difficulty to remove the product from reaction glassware. Characterization is consistent with that reported previously.[62] $^1$H (400 MHz; 298 K; $CDCl_3$): $\delta$ (ppm) 9.18 (br s, 1H, N*H*), 3.47 (m, 4H, $NCH_2CH_2CH_2CH_2$, $NHCH_2$), 3.37 (m, 2H, $NCH_2CH_2CH_2NH$), 2.70 (m, 2H, $CH_2C(N)NH$), 2.00 (quin., 2H, $^3J_{H-H}$ = 11.7 Hz, $NCH_2CH_2CH_2NH$), 1.77−1.63 (m, 6H, $NCH_2CH_2CH_2CH_2$). $^{13}$C: $\delta$ (ppm) 166.39 ($CH_2C(N)NH$), 120.54 (q, $CF_3$), 54.69 ($NCH_2CH_2CH_2NH$), 48.70 ($NCH_2CH_2CH_2CH_2$), 38.29 ($NHCH_2$), 32.92 ($CH_2C(N)NH$), 28.90 ($NCH_2CH_2CH_2NH$), 26.58 ($NCH_2CH_2CH_2CH_2$), 23.79 ($NCH_2CH_2CH_2CH_2$), 19.36($NCH_2CH_2CH_2CH_2$).

*ABCO:MSA (1:1) Salt.* ABCO:MSA (1:1) salt was synthesized as reported previously.[63] ABCO (0.111 g, 1.0 mmol), acetone (23 mL), and MSA (96.1 mg, 64.9 $\mu$L, 1.0 mmol) were mixed in a Schlenk flask. The mixture was heated at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. Crystals were collected, washed with acetone, and dried under vacuum at room temperature overnight (0.089 g, 43%). Characterization is consistent with that reported previously.[63] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 9.18 (br s, 1H, N*H*), 3.21 (m, 6H, $CH_2CH_2NH$), 2.34 (s, 3H, $CH_3$), 2.01 (m, 1H, $CH_3CH(CH_3)CH_3$), 1.78 (m, 6H, $CHCH_2CH_2$). $^{13}$C: $\delta$ (ppm) 45.69 ($CH_2CH_2NH$), 39.73 ($CH_3CH(CH_3)CH_3$), 22.39 ($CHCH_2CH_2$), 18.74 ($CH_3$).

*DMAP:TfOH (1:1) Salt.* DMAP:TfOH (1:1) salt was synthesized as reported previously.[64] Acetone (5 mL), DMAP (0.611 g, 5 mmol), and TfOH (0.750 g, 0.442 mL, 5 mmol) were mixed and heated at 65−70 °C under $N_2$ for 10 min in a Schlenk flask to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator, and the crystals were collected. The crystals were further treated by adding acetone (4 mL) and heating in a Schlenk flask at 45 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized again in the refrigerator. These crystals were collected and dried under vacuum at room temperature overnight (0.5191 g, 38%). Characterization is consistent with that reported previously.[64] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 13.35 (br s, 1H, N*H*), 8.20 (dd, 2H, $^3J_{H-H}$ = 7.6 Hz, CHC*H*NH), 6.98 (dd, 2H, $^3J_{H-H}$ = 7.6 Hz, CC*H*CH), 3.18 (s, 6H, $NCH_3$). $^{13}$C: $\delta$ (ppm) 156.97 ($CH_3NCCH$), 139.15 (CHCHN), 120.69 (q, $CF_3$), 106.95 (C*C*HCH), 39.63 ($NCH_3$).

*DMAP:BSA (1:1) Salt.* Acetone (25 mL), DMAP (0.611 g, 5 mmol), and BSA (0.791 g, 5 mmol) were mixed and heated at 65−70 °C under $N_2$ for 1 h, but the resultant solid was not soluble. The mixture was then cooled in the refrigerator, and the solid was collected. The solid was further treated by adding acetone (80 mL) and heating in a round-bottom flask at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. Crystals were collected, washed with acetone, and dried under vacuum at room temperature overnight (0.849 g, 61%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 13.19 (br s, 1H, N*H*), 8.21 (d, 2H, $^3J_{H-H}$ = 7.7 Hz, CHC*H*NH), 7.61 (m, 2H, SCC*H*), 7.31 (m, 3H, CCHC*H*C*H*), 6.98 (d, $^3J_{H-H}$ = 7.7 Hz, C*H*CHNH), 3.17 (s, 6H, $CH_3$). $^{13}$C: $\delta$ (ppm) 156.94 ($CH_3NCCH$), 148.27 (CHCHNH), 139.11 (SCCH), 128.42 (CCHCHCH), 127.65 (CCHCHCH), 125.48 (CHCHNH), 106.96 (CCHCHCH), 39.62 ($CH_3$). MS (ESI): $m/z$ 123.10 ($DMAPH^+$), 157.03 ($BSA^-$). FT-IR (ATR): max/cm$^{-1}$ 3211 (NH or OH), 3048 (CH), 2906 ($CH_2$), 2768 ($NCH_3$), 2682 ($N^+$−H), 1639, 1602, 1557 (C═C), 1472, 1442, 1397, 1211, 1207, 1162, 1118, 1066, and 1028 ($SO_2$). Anal. Calcd for $C_{13}H_{16}N_2O_3S$: C 55.7; H 5.75; N 10.0; S 11.4%. Found: C 55.8; H 5.74; N 10.25; S 11.4%.

*DMAP:MSA (1:1) Salt.* DMAP:MSA (1:1) salt was synthesized as reported previously.[26,64] DMAP (2.00 g, 16.4 mmol), acetone (60 mL), and MSA (1.57 g, 1.06 mL, 16.4 mmol) were mixed in a Schlenk flask at 65−70 °C under $N_2$ for 1 h, but the resultant solid was not soluble. The mixture was cooled to room temperature, and the solid was collected and washed with acetone. The crystals were further treated by adding acetone (220 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 1.5 h, but the solid was still insoluble. The mixture was then cooled in the refrigerator. The solid was collected, washed with acetone, and dried under vacuum at room temperature overnight (2.39 g, 67%). Characterization is consistent with that reported previously.[26,64] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 13.18 (br s, 1H, N*H*), 8.22 (dd, 2H, $^3J_{H-H}$ = 7.6 Hz, CHC*H*NH), 6.98 (dd, 2H, $^3J_{H-H}$ = 7.6 Hz, CC*H*CH), 3.18 (s, 6H, $NCH_3$), 2.30 (s, 3H, $SCH_3$). $^{13}$C: $\delta$ (ppm) 156.96 ($CH_3NCCH$), 139.15 (CHCHNH), 106.98 (CCHCH), 39.77 ($NCH_3$), 39.63 ($SCH_3$).

*DMAP:p-TSA (1:1) Salt.* DMAP:*p*-TSA (1:1) salt was synthesized as reported previously.[65−67] Acetone (20 mL), DMAP (0.611 g, 5 mmol), and *p*-TSA monohydrate (0.951 g, 5 mmol) were mixed and heated at 65−70 °C under $N_2$ for 30 min, but the resultant solid was not soluble. The mixture was then cooled in the refrigerator, and the


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solid was collected. The solid was further treated by adding acetone (100 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 30 min, but the solid was not soluble. The mixture was then cooled in the refrigerator. The solid was collected and dried under vacuum at room temperature overnight (1.18 g, 80%). Characterization is consistent with that reported previously.[65−67] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 13.21 (br s, 1H, N*H*), 8.21 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, CHC*H*NH), 7.50 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, NCC*H*CH), 7.11 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, SCC*H*CH), 6.97 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, CHC*H*CCH$_3$), 3.17 (s, 6H, NC*H*$_3$), 2.28 (s, 3H, SC*H*$_3$). $^{13}$C: $\delta$ (ppm) 156.93 (CH$_3$NCCH), 145.59 (CHCCH$_3$), 139.11 (CHCHN), 137.70 (SCCH), 128.09 (CHCHCCH$_3$), 125.48 (SCCHCH), 106.96 (CCHCH), 39.61 (NCH$_3$), 20.77 (CCH$_3$).

*DMAP:TPA (2:1) Salt.* DMAP:TPA (2:1) salt was synthesized as reported previously.[68] TPA (0.831 g, 5 mmol), DMAP (1.22 g, 10 mmol), and methanol (15 mL) were mixed. Methanol (60 mL) was added, and the mixture was heated at 60 °C to form a transparent and homogeneous solution. The mixture was then cooled in the refrigerator. The crystal was filtered, washed with methanol, and dried under vacuum at room temperature overnight (1.36 g, 67%). Characterization is consistent with that reported previously.[68] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 8.11 (dd, 4H, $^3J_{H-H}$ = 5.0 Hz, 1.6 Hz, NHC*H*), 8.00 (s, 4H, C*H*CCOO), 6.63 (dd, 4H, $^3J_{H-H}$ = 5.0 Hz, 1.6 Hz, C*H*CNCH$_3$), 2.97 (s, 12H, CH$_3$). N*H* was not observed. $^{13}$C: $\delta$ (ppm) 166.97 (COO), 154.28 (CH$_3$NCCH), 148.21 (CHCHNH), 135.24 (CCOO), 129.28 (CHCCOO), 106.74 (CHCNCH$_3$), 38.72 (CH$_3$).

*DMAP:BA (1:1) Salt.* DMAP:BA (1:1) salt was synthesized as reported previously.[29] Diethyl ether (12 mL) and BA (0.611 g, 5 mmol) were added to a Schlenk flask. DMAP (0.611 g, 5 mmol) was added to the stirred solution forming white solids. The solids were filtered, washed with diethyl ether, and dried under vacuum at room temperature overnight (0.925 g, 76%). Characterization is consistent with that reported previously.[29] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 8.13 (dd, 2H, $^3J_{H-H}$ = 5.0 Hz, $^4J_{H-H}$ = 1.6 Hz, CHC*H*NH), 7.95 (m, 2H, CC*H*CH), 7.58 (t, 1H, $^3J_{H-H}$ = 7.4 Hz, CCHCH*C*H), 7.47 (t, 2H, $^3J_{H-H}$ = 7.4 Hz, CCHC*H*CH), 6.63 (dd, 2H, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 1.6 Hz, C*H*CHNH), 2.97 (s, 6H, CH$_3$). N*H* was not observed. $^{13}$C: $\delta$ (ppm) 167.73 (COOH), 154.33 (CH$_3$NCCH), 148.03 (CHCHNH), 132.37 (CCOOH), 131.95 (CCHCHCH), 129.23 (CCHCHCH), 128.41 (CCHCHCH), 106.73 (CHCHNH), 38.72 (CH$_3$).

*DMAP:BHET (2:1) Salt.* BHET (1.27 g, 5 mmol), DMAP (1.22 g, 10 mmol), and THF (15 mL) were mixed. The solution was cooled in the refrigerator, but solids were not formed. The solution was dripped into diethyl ether (150 mL), and it was cooled in the refrigerator forming crystals. The crystal was filtered and dried under vacuum at room temperature overnight (0.691 g, 28%). The chemical structure was identified by NMR, and the crystal was BHET. DMAP:BHET (2:1) salt was not formed.

*DABCO:MSA (1:2) Salt.* DABCO:MSA (1:2) salt was synthesized as reported previously.[69] DABCO (0.808 g, 7.2 mmol), acetone (10 mL), and MSA (1.45 g, 0.982 mL, 15.1 mmol) were mixed in a round-bottom flask. Acetone (190 mL) was added and the mixture heated at 65−70 °C under $N_2$ for 40 min, but the resultant solid was insoluble. The mixture was cooled in the refrigerator. The solid was collected, washed with acetone, and dried under vacuum at room temperature overnight (1.90 g, 87%). Characterization is consistent with that reported previously.[69] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 3.55 (s, 12H, NHC*H*$_2$C*H*$_2$NH) 2.40 (s, 6H, C*H*$_3$). N*H* was not observed. $^{13}$C: $\delta$ (ppm) 42.91 (NHCH$_2$CH$_2$NH), 39.71 (CH$_3$).

*NMI:TfOH (1:1) Salt.* NMI:TfOH (1:1) salt was synthesized as reported previously.[70,71] Dichloromethane (3 mL), TfOH (0.750 g, 0.442 mL, 5 mmol), and NMI (0.411 g, 0.399 mL, 5 mmol) were mixed. Solids were formed. The solids were collected, washed with dichloromethane, and dried under vacuum at room temperature overnight (0.697 g, 60%). Characterization is consistent with that reported previously.[70,71] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 14.12 (br s, 1H, N*H*), 9.03 (s, 1H, NHC*H*N), 7.67 (m, 2H, NHC*H*C*H*NCH$_3$), 3.86 (s, 3H, NC*H*3). $^{13}$C: $\delta$ (ppm) 135.80 (NHCHN), 123.15 (CHCHNCH$_3$), 120.69 (q, CF$_3$), 119.74 (CHCHNH), 35.41 (NCH$_3$).

*NMI:BSA (1:1) Salt.* NMI:TfOH (1:1) salt was synthesized as reported previously.[72] Acetone (5 mL), BSA (0.791 g, 5 mmol), and NMI (0.411 g, 0.399 mL, 5 mmol) were mixed, but solids were not formed. Dichloromethane (25 mL) was added, but solids were still not formed. The solution was dripped into diethyl ether (75 mL) forming solids. The mixture was cooled in the refrigerator, and the solids were collected. The solids were further treated by adding acetone (5 mL) and mixing under $N_2$; then the solution was dripped into diethyl ether (100 mL) forming solids. The solids were filtered and dried under vacuum at room temperature overnight (0.530 g, 44%). Characterization is consistent with that reported previously.[72] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 14.18 (br s, 1H, N*H*), 9.06 (s, 1H, NHC*H*N), 7.69 (t, 1H, $^3J_{H-H}$ = 1.6 Hz, CHC*H*NCH$_3$), 7.66 (t,1H, $^3J_{H-H}$ = 1.6 Hz, CHC*H*NH), 7.62 (m, 2H, SCC*H*), 7.32 (m, 3H, CCHC*H*C*H*), 3.86 (s, 3H, C*H*3). $^{13}$C: $\delta$ (ppm) 148.17 (SCCH), 135.83 (NHCHN), 128.50 (CCHCHCH), 127.69 (CCHCHCH), 125.46 (CCHCHCH), 123.16 (CHCHNCH$_3$), 119.73 (CHCHNH), 35.39 (NCH$_3$).

*NMI:MSA (1:1) Salt.* NMI:MSA (1:1) salt was synthesized as reported previously.[73−75] NMI (1.18 g, 1.148 mL, 14.4 mmol), MSA (1.38 g, 0.932 mL, 14.4 mmol), and acetone (20 mL) were mixed in a Schlenk flask. A white solid was formed. Acetone (180 mL) was added and the mixture heated at 65−70 °C under $N_2$ for 30 min, but the resultant solid was not soluble. The mixture was then cooled in the refrigerator, and the solid was collected. The solid was further treated by adding acetone (400 mL) and heating in a Schlenk flask at 65−70 °C under $N_2$ for 30 min, but the solid was not soluble. The mixture was then cooled in the refrigerator. The solid was collected, washed with acetone, and dried under vacuum at room temperature overnight (1.93 g, 75%). Characterization is consistent with that reported previously.[73−75] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 9.07 (s, 1H, NHC*H*N), 7.70 (t, 1H, $^3J_{H-H}$ = 1.6 Hz, CHC*H*NCH$_3$), 7.66 (t, 1H, $^3J_{H-H}$ = 1.6 Hz, CHC*H*NH), 3.87 (s, 3H, NC*H*3), 2.37 (s, 3H, SCH$_3$). N*H* was not observed. $^{13}$C: $\delta$ (ppm) 135.88 (NHCHN), 123.18 (CHCHNCH$_3$), 119.76 (CHCHNH), 39.80 (SCH$_3$), 35.39 (NCH$_3$).

*DMA:TfOH (1:1) Salt.* DMA:TfOH (1:1) salt was synthesized as reported previously.[76] Acetone (5 mL), DMA (0.606 g, 0.634 mL, 5 mmol), and TfOH (0.750 g, 0.442 mL, 5 mmol) were mixed under $N_2$ in a Schlenk flask. The mixture was cooled in the refrigerator, but solids were not formed. The solution was dripped into diethyl ether (50 mL) forming a two-layer solution. The lower layer was collected and washed with diethyl ether. *n*-Hexane (5 mL) was added forming a two-layer solution. The mixture was cooled in the refrigerator, but solids were not formed. The lower layer was collected and dried under vacuum at room temperature overnight to afford a solid (0.304 g, 22%). Characterization is consistent with that reported previously.[76] $^1$H (400 MHz; 298 K; CDCl$_3$): $\delta$ (ppm) 11.08 (br s, 1H, N*H*), 7.63−7.49 (m, 5H, C*H*C*H*C*H*CN), 3.30 (d, 6H, NC*H*$_3$). $^{13}$C: $\delta$ (ppm) 144.24 (CHCNH), 131.03 (CHCHCHCN), 130.93 (CHCHCH), 120.46 (q, CF$_3$), 120.33 (CHC*H*CN), 47.48 (NC*H*$_3$).

*DMA:MSA (1:1) Salt.* DMA:MSAH (1:1) salt was synthesized as reported previously.[77] DMA (1.74 g, 1.825 mL, 14.4 mmol), acetone (20 mL), and MSA (1.38 g, 0.932 mL, 14.4 mmol) were mixed in a round-bottom flask. The solid was formed in 15 min. Acetone (30 mL) was added, and the mixture was heated at 65−70 °C under $N_2$ for 30 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator and collected. The crystals were further treated by adding acetone (40 mL) and heating in a round-bottom flask at 65−70 °C under $N_2$ for 20 min to form a transparent and homogeneous solution. The mixture was then recrystallized in the refrigerator. Crystals were collected and dried under vacuum at room temperature overnight (2.22 g, 71%). Characterization is consistent with that reported previously.[77] $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.48−7.30 (m, 5H, C*H*C*H*C*H*CN), 3.13 (s, 6H, NC*H*$_3$), 2.39 (s, 3H, SC*H*$_3$). N*H* was not observed. $^{13}$C: $\delta$ (ppm) 144.25 (CHCNH), 130.03


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(CHCHCHCN), 127.65 (CHCHCH), 119.68 (CHC*H*CN), 45.15 (NC$H_3$), 39.72 (SC$H_3$).

*BEMP:TfOH (1:1) Salt.* Acetone (2 mL), BEMP (0.549 g, 0.579 mL, 2 mmol), and TfOH (0.300 g, 0.177 mL, 2 mmol), were mixed under $N_2$ in a Schlenk flask. The mixture was cooled in the refrigerator, but solids were not formed. The solution was dripped into diethyl ether (20 mL) forming solids. The solids were filtered. The solids were further treated by adding acetone (1.5 mL), mixed under $N_2$, and cooled in the refrigerator. The solution was dripped into diethyl ether (20 mL) forming solids. The solids were filtered, washed with diethyl ether, and dried under vacuum at room temperature overnight (0.708 g, 83%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 4.87 (d, 1H, $^3J_{H-H}$ = 10.1 Hz, N*H*), 3.19 (td, 4H, $^3J_{H-H}$ = 5.8 Hz, $^3J_{H-H}$ = 10.5 Hz, $CH_3NCH_2CH_2$), 3.04 (qd, 4H, $^3J_{H-H}$ = 7.1 Hz, $^3J_{H-H}$ = 11.3 Hz, $NCH_2CH_3$), 2.60 (s, 6H, $NCH_3$), 1.88 (tt, 2H, $^3J_{H-H}$ = 14.7 Hz, $^3J_{H-H}$ = 8.1 Hz, $CH_2CH_2CH_2$), 1.27 (d, 9H, $J_{H-H}$ = 0.8 Hz, $NHCCH_3$), 1.09 (t, 6H, $^3J_{H-H}$ = 7.1 Hz, $NCH_2CH_3$). $^{13}$C: $\delta$ (ppm) 120.68 (quin, $CF_3$), 52.54 (d, $CH_3NCH_2CH_2$), 49.70 (d, $NCH_2CH_3$), 38.93 ($CH_2CH_2CH_2$), 34.91 (d, $NHCCH_3$), 30.44 (d, $NCH_3$), 23.91 (d, $NHCCH_3$), 13.25 (d, $NCH_2CH_3$). MS (ESI): *m*/*z* 275.27 ($BEMPH^+$), 149.04 ($TfO^-$). FT-IR (ATR): max/cm$^{-1}$ 3249 (NH or OH), 2962 and 2958 ($CH_3$, $CH_2$), 2872 ($N^+$−H), 1472 and 1416 ($SO_2$), 1382 and 1367 ($C(CH_3)_3$), 1274, 1248, 1218, 1144, 1051, and 1021 ($SO_2$, $CF_3$). Anal. Calcd for $C_{14}H_{32}F_3N_4O_3PS$: C 39.6; H 7.6; N 13.2; S 7.55%. Found: C 39.6; H 7.6; N 13.3; S 7.5%.

*BEMP:MSA (1:1) Salt.* Acetone (2 mL), methanesulfonic acid (MSA) (0.192 g, 0.130 mL, 2 mmol), and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) (0.549 g, 0.579 mL, 2 mmol) were mixed under $N_2$ in a Schlenk flask. The mixture was cooled in the refrigerator, but solids were not formed. The solution was dripped into diethyl ether (20 mL) forming a two-layer solution. The lower layer was collected and washed with diethyl ether. The solution was dried under vacuum at room temperature overnight to afford a solid (0.499 g, 67%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 4.92 (d, 1H, $^3J_{H-H}$ = 9.9 Hz, N*H*), 3.19 (dt, 4H, $^3J_{H-H}$ = 5.9 Hz, $^3J_{H-H}$ = 10.5 Hz, $^3J_{H-H}$ = 5.8 Hz, $CH_3NCH_2CH_2$), 3.04 (dq, 4H, $^3J_{H-H}$ = 7.1 Hz, $^3J_{H-H}$ = 11.3 Hz, $NCH_2CH_3$), 2.60 (d, 6H, $^3J_{H-H}$ = 10.3 Hz, $NCH_3$), 2.29 (s, 3H, $SCH_3$), 1.88 (m, 2H, $CH_2CH_2CH_2$), 1.27 (d, 9H, $J_{H-H}$ = 0.8 Hz, $NHCCH_3$), 1.08 (t, 6H, $^3J_{H-H}$ = 7.1 Hz, $NCH_2CH_3$). $^{13}$C: $\delta$ (ppm) 52.54 (d, $CH_3NCH_2CH_2$), 49.70 (d, $NCH_2CH_3$), 39.77 ($SCH_3$), 38.93 ($CH_2CH_2CH_2$), 34.93 (d, $NHCCH_3$), 30.46 (d, $NCH_3$), 23.93 (d, $NHCCH_3$), 13.26 (d, $NCH_2CH_3$). MS (ESI): *m*/*z* 275.27 ($BEMPH^+$), 95.02 ($MSA^-$). FT-IR (ATR): max/cm$^{-1}$ 3163 (OH), 2958 and 2925 ($CH_3$, $CH_2$), 2869 ($N^+$−H), 1479, 1464, and 1427 ($SO_2$), 1386 and 1364 ($C(CH_3)_3$), 1293, 1263, 1181, 1155, 1128, and 1102 ($SO_2$). Anal. Calcd for $C_{14}H_{35}N_4O_3PS$: C 45.4; H 9.5; N 15.1; S 8.65%. Found: C 45.5; H 9.6; N 15.2; S 8.4%.

*BEMP:TFA (1:1) Salt.* Acetone (2 mL), BEMP (0.549 g, 0.579 mL, 2 mmol), and TFA (0.228 g, 0.153 mL, 2 mmol) were mixed under $N_2$ in a Schlenk flask. The mixture was cooled in the refrigerator, but solids were not formed. The solution was dripped into diethyl ether (40 mL), but solids were not formed. The solvents were removed by a vacuum pump, and then diethyl ether (10 mL) was added forming solids. The solids were filtered and dried under vacuum at room temperature overnight (0.490 g, 63%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 4.99 (d, 1H, $^3J_{H-H}$ = 10.2 Hz, N*H*), 3.19 (td, 4H, $^3J_{H-H}$ = 5.9 Hz, $^3J_{H-H}$ = 10.4 Hz, $CH_3NCH_2CH_2$), 3.04 (qd, 4H, $^3J_{H-H}$ = 7.1 Hz, $^3J_{H-H}$ = 11.3 Hz, $NCH_2CH_3$), 2.60 (d, 6H, $^3J_{H-H}$ = 10.3 Hz, $NCH_3$), 1.88 (m, 2H, $CH_2CH_2CH_2$), 1.27 (d, 9H, $J_{H-H}$ = 1.0 Hz, $NHCCH_3$), 1.09 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, $NCH_2CH_3$). $^{13}$C: $\delta$ (ppm) 157.59 (q, $CF_3CO_2$), 117.42 (quin, $CF_3$), 52.53 (d, $CH_3NCH_2CH_2$), 49.70 (d, $NCH_2CH_3$), 38.88 ($CH_2CH_2CH_2$), 34.92 (d, $NHCCH_3$), 30.44 (d, $NCH_3$), 23.92 (d, $NHCCH_3$), 13.23 (d, $NCH_2CH_3$). MS (ESI): *m*/*z* 275.27 ($BEMPH^+$), 112.96 ($TFA^-$). FT-IR (ATR): max/cm$^{-1}$ 3062 (OH), 2962 and 2928 ($CH_3$, $CH_2$), 2861 ($N^+$−H), 1684 (COO), 1475 and 1434 ($SO_2$), 1390, 1378, and 1364 ($C(CH_3)_3$), 1341, 1285, 1263, 1226, 1192, 1155, 1106, 1051, and 1017 ($SO_2$, $CF_3$). Anal. Calcd for $C_{15}H_{32}F_3N_4O_2P$: C 46.4; H 8.3; N 14.4%. Found: C 46.7; H 8.3; N 14.6%.

*BEMP:DPP (1:1) Salt.* Diphenyl phosphate (DPP) (0.50 g, 2 mmol), 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) (0.549 g, 0.579 mL, 2 mmol), and acetone (2 mL) were mixed. The solution was dripped into diethyl ether (20 mL) forming a two-layer solution. The lower layer was collected, washed with diethyl ether, and dried under vacuum at room temperature overnight (0.410 g, 39%). $^1$H (400 MHz; 298 K; DMSO-$d_6$): $\delta$ (ppm) 7.20 (t, 4H, $^3J_{H-H}$ = 7.8 Hz, CCHC*H*CH), 7.12 (m, 4H, OCCH), 6.94 (t, 2H, $^3J_{H-H}$ = 7.2 Hz, CCHCHC*H*), 5.10 (d, 1H, $^3J_{H-H}$ = 10.2 Hz, N*H*), 3.17 (td, 4H, $^3J_{H-H}$ = 5.8 Hz, $^3J_{H-H}$ = 10.6 Hz, $CH_3NCH_2CH_2$), 3.03 (qd, 4H, $^3J_{H-H}$ = 7.1 Hz, $^3J_{H-H}$ = 11.3 Hz, $NCH_2CH_3$), 2.58 (d, 6H, $^3J_{H-H}$ = 10.3 Hz, $NCH_3$), 1.87 (m, 2H, $^3J_{H-H}$ = 5.9 Hz, $CH_2CH_2CH_2$), 1.26 (d, 9H, $^3J_{H-H}$ = 0.9 Hz, $NHCCH_3$), 1.07 (t, 6H, $^3J_{H-H}$ = 7.1 Hz, $NCH_2CH_3$). $^{13}$C: $\delta$ (ppm) 154.05 (d, $CH_2C(O)CH_2$), 128.70(CCHCHCH), 121.59 (CCHCHCH), 119.84 (d, CCHCHCH), 52.50 (d, $CH_3NCH_2CH_2$), 49.69 (d, $NCH_2CH_3$), 38.92 ($CH_2CH_2CH_2$), 34.93 (d, $NHCCH_3$), 30.44 (d, $NCH_3$), 23.92 (d, $NHCCH_3$), 13.25 (d, $NCH_2CH_3$). MS (ESI): *m*/*z* s75.39 ($BEMPH^+$), 249.03 ($DPP^-$). FT-IR (ATR): max/cm$^{-1}$ 3055 (OH or CH), 2962, 2925, and 2887 ($CH_3$, $CH_2$), 2865 ($N^+$−H), 1591 and 1487 (C═C), 1378 and 1364 ($C(CH_3)_3$), 1278 (P═O), 1256, 1215, 1159, 1129, 1092, 1051 (PO−Aryl). Anal. Calcd for $C_{25}H_{42}N_4O_4P_2$: C 57.2; H 8,1; N 10.7%. Found: C 57.5; H 8.0; N 10.4%.

**General Procedure for Polymerization Reaction.** BHET (0.5 g) and a salt catalyst (2.5−5 mol %) were added to a round-bottom flask simultaneously. Then, the mixture was heated at 270 °C in a heating block for 1 h under $N_2$ while stirring with a magnetic stirrer at a rate of 300 rpm. Vacuum was then applied, and the mixture was maintained at 270 °C for an additional 4 h. The reaction mixture was cooled to room temperature, and a mixture of chloroform and trifluoroacetic acid (8:1) (5 mL) was added to solubilize the crude polymer. Methanol (50 mL) was then added to the reaction flask, while stirring, to precipitate the PET which was collected by filtration and dried under vacuum at room temperature overnight.

**General Procedure for Depolymerization Reaction.** As-synthesized poly(ethylene terephthalate) (PET), which includes embedded salt catalyst (5 mol %), was combined with EG (20 equiv) in a 20 mL scintillation vial. The vial was sealed and heated at 180 °C for 24.5 h or until the PET was fully dissolved and the reaction mixture was homogeneous. The solution was cooled to ambient temperature and filtered. Then, $H_2O$ (ca. 10 mL) was added to the vial and stored at 4 °C overnight. The precipitated BHET was recovered from the crude mixture via filtration and dried at room temperature for 24 h.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c01410.

Thermogravimetric analysis, NMR spectra, molecular wight and colorimetric data (PDF)

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### Notes
The authors declare no competing financial interest.

## ■ ABBREVIATIONS

PPS, poly(phenylene sulfide); PET, poly(ethylene terephthalate; PBT, poly(butylene terephthalate); PA, polyamide; BHET, bis(2-hydroxyethyl) terephthalate; DEG, diethylene glycol; ROP, ring-opening polymerization; DMAP, *N,N*-dimethyl-4-aminopyridine; TBD, 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; BEMP, 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine; BA, benzoic acid; TFA, trifluoroacetic acid; MSA, methanesulfonic acid; TSA, *p*-toluenesulfonic acid.

## ■ REFERENCES

(1) Lopez, L. C.; Wilkes, G. L. Poly(p-phenylene sulfide) — An overview of an important engineering thermoplastic. *J. Macromol. Sci. C* **1989**, *29*, 83−151.
(2) Hill, H. W., Jr.; Brady, D. G. Properties, environmental stability, and molding characteristics of polyphenylene sulfide. *Polym. Eng. Sci.* **1976**, *16*, 831−835.
(3) Rahate, A. S.; Nemade, K. R.; Waghuley, S. A. Polyphenylene sulfide (PPS): State of the art and applications. *Rev. Chem. Eng.* **2013**, *29*, 471−489.
(4) Lepoittevin, B.; Roger, P. Poly(ethylene terephthalate). *Handbook of Engineering and Speciality Thermoplastics* **2011**, 97−126.
(5) Aharoni, S. M. Industrial-Scale Production of Polyesters, Especially Poly(Ethylene Terephthalate). *Handbook of Thermoplastic Polyesters* **2002**, 59−103.
(6) Antić, V. V.; Pergal, M. V. Poly(butylene terephthalate) — Synthesis, Properties, Application. *Handbook of Engineering and Speciality Thermoplastics* **2011**, 127−180.
(7) Radusch, H.-J. Poly(Butylene Terephthalate). *Handbook of Thermoplastic Polyesters* **2002**, 389−419.
(8) Visakh, P. M.; Thomas, S. Engineering and Specialty Thermoplastics: Nylons: State of Art, New Challenges and Opportunities. *Handbook of Engineering and Specialty Thermoplastics* **2011**, 1−9.
(9) García, J. M.; García, F. C.; Serna, F.; de la Peña, J. L. Aromatic Polyamides (Aramids). *Handbook of Engineering and Specialty Thermoplastics* **2011**, 141−181.
(10) Gupta, V. B.; Bashir, Z. PET Fibers, Films, and Bottles: Sections 1−4.13. *Handbook of Thermoplastic Polyesters* **2002**, 317−361.
(11) Gupta, V. B.; Bashir, Z. PET Fibers, Films, and Bottles: Sections 5−7. *Handbook of Thermoplastic Polyesters* **2002**, 362−388.
(12) Bossion, A.; Heifferon, K. V.; Meabe, L.; Zivic, N.; Taton, D.; Hedrick, J. L.; Long, T. E.; Sardon, H. Opportunities for organocatalysis in polymer synthesis via step-growth methods. *Prog. Polym. Sci.* **2019**, *90*, 164−210.
(13) Shah, T. H.; Bhatty, J. I.; Gamlen, G. A.; Dollimore, D. Aspects of the chemistry of poly(ethylene terephthalate): 5. Polymerization of bis(hydroxyethyl)terephthalate by various metallic catalysts. *Polymer* **1984**, *25*, 1333−1336.
(14) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. Organocatalytic Ring-Opening Polymerization. *Chem. Rev.* **2007**, *107*, 5813−5840.
(15) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. Organocatalysis: Opportunities and Challenges for Polymer Synthesis. *Macromolecules* **2010**, *43*, 2093−2107.
(16) Dove, A. P. Organic Catalysis for Ring-Opening Polymerization. *ACS Macro Lett.* **2012**, *1*, 1409−1412.
(17) Ottou, W. N.; Sardon, H.; Mecerreyes, D.; Vignolle, J.; Taton, D. Update and challenges in organo-mediated polymerization reactions. *Prog. Polym. Sci.* **2016**, *56*, 64−115.
(18) Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M. Catalysis as an Enabling Science for Sustainable Polymers. *Chem. Rev.* **2018**, *118*, 839−885.
(19) Basterretxea, A.; Jehanno, C.; Mecerreyes, D.; Sardon, H. Dual Organocatalysts Based on Ionic Mixtures of Acids and Bases: A Step Toward High Temperature Polymerizations. *ACS Macro Lett.* **2019**, *8*, 1055−1062.
(20) Jehanno, C.; Flores, I.; Dove, A. P.; Müller, A. J.; Ruipérez, F.; Sardon, H. Organocatalysed depolymerisation of PET in a fully sustainable cycle using thermally stable protic ionic salt. *Green Chem.* **2018**, *20*, 1205−1212.
(21) Fukushima, K.; Coady, D. J.; Jones, G. O.; Almegren, H. A.; Alabdulrahman, A. M.; Alsewailem, F. D.; Horn, H. W.; Rice, J. E.; Hedrick, J. L. Unexpected efficiency of cyclic amidine catalysts in depolymerizing poly(ethylene terephthalate). *J. Polym. Sci. A Polym. Chem.* **2013**, *51*, 1606−1611.
(22) Jehanno, C.; Demarteau, J.; Mantione, D.; Arno, M. C.; Ruipérez, F.; Hedrick, J. L.; Dove, A. P.; Sardon, H. Selective Chemical Upcycling of Mixed Plastics Guided by a Thermally Stable Organocatalyst. *Angew. Chem., Int. Ed.* **2021**, *60*, 6710−6717.
(23) Li, H.; Zhang, S.; Jiao, J.; Jiao, Z.; Kong, L.; Xu, J.; Li, J.; Zuo, J.; Zhao, X. Controlled Synthesis of Polylactides Using Biogenic Creatinine Carboxylate Initiators. *Biomacromolecules* **2009**, *10*, 1311−1314.
(24) Coulembier, O.; Josse, T.; Guillerm, B.; Gerbaux, P.; Dubois, P. An imidazole-based organocatalyst designed for bulk polymerization of lactide isomers: inspiration from Nature. *Chem. Commun.* **2012**, *48*, 11695−11697.
(25) Kadota, J.; Pavlović, D.; Hirano, H.; Okada, A.; Agari, Y.; Bibal, B.; Deffieux, A.; Peruch, F. Controlled bulk polymerization of l-lactide and lactones by dual activation with organo-catalytic systems. *RSC Adv.* **2014**, *4*, 14725−14732.
(26) Kadota, J.; Pavlović, D.; Desvergne, J.-P.; Bibal, B.; Peruch, F.; Deffieux, A. Ring-Opening Polymerization of l-Lactide Catalyzed by an Organocatalytic System Combining Acidic and Basic Sites. *Macromolecules* **2010**, *43*, 8874−8879.
(27) Guillerm, B.; Lemaur, V.; Ernould, B.; Cornil, J.; Lazzaroni, R.; Gohy, J.-F.; Dubois, P.; Coulembier, O. A one-pot two-step efficient metal-free process for the generation of PEO-b-PCL-b-PLA amphiphilic triblock copolymers. *RSC Adv.* **2014**, *4*, 10028−10038.
(28) Wei, F.; Zhu, H.; Li, Z.; Wang, H.; Zhu, Y.; Zhang, L.; Yao, Z.; Luo, Z.; Zhang, C.; Guo, K. Food Sweetener Saccharin in Binary Organocatalyst for Bulk Ring-Opening Polymerization of Lactide. *Adv. Synth. Catal.* **2019**, *361*, 1335−1347.
(29) Coady, D. J.; Fukushima, K.; Horn, H. W.; Rice, J. E.; Hedrick, J. L. Catalytic insights into acid/base conjugates: highly selective bifunctional catalysts for the ring-opening polymerization of lactide. *Chem. Commun.* **2011**, *47*, 3105−3107.
(30) Coderre, D. N.; Fastnacht, K. V.; Wright, T. J.; Dharmaratne, N. U.; Kiesewetter, M. K. H-Bonding Organocatalysts for Ring-Opening Polymerization at Elevated Temperatures. *Macromolecules* **2018**, *51*, 10121−10126.
(31) Shi, C.-X.; Guo, Y.-T.; Wu, Y.-H.; Li, Z.-Y.; Wang, Y.-Z.; Du, F.-S.; Li, Z.-C. Synthesis and Controlled Organobase-Catalyzed Ring-Opening Polymerization of Morpholine-2,5-Dione Derivatives and Monomer Recovery by Acid-Catalyzed Degradation of the Polymers. *Macromolecules* **2019**, *52*, 4260−4269.

(32) Wang, X.; Cui, S.; Li, Z.; Kan, S.; Zhang, Q.; Zhao, C.; Wu, H.; Liu, J.; Wu, W.; Guo, K. A base−conjugate-acid pair for living/controlled ring-opening polymerization of trimethylene carbonate through hydrogen-bonding bifunctional synergistic catalysis. *Polym. Chem.* **2014**, *5*, 6051−6059.
(33) García-Argüelles, S.; García, C.; Serrano, M. C.; Gutiérrez, M. C.; Ferrer, M. L.; del Monte, F. Near-to-eutectic mixtures as bifunctional catalysts in the low-temperature-ring-opening-polymerization of ε-caprolactone. *Green Chem.* **2015**, *17*, 3632−3643.
(34) Basterretxea, A.; Gabirondo, E.; Jehanno, C.; Zhu, H.; Flores, I.; Müller, A. J.; Etxeberria, A.; Mecerreyes, D.; Coulembier, O.; Sardon, H. Polyether Synthesis by Bulk Self-Condensation of Diols Catalyzed by Non-Eutectic Acid−Base Organocatalysts. *ACS Sustain. Chem. Eng.* **2019**, *7*, 4103−4111.
(35) Basterretxea, A.; Gabirondo, E.; Flores, I.; Etxeberria, A.; Gonzalez, A.; Müller, A. J.; Mecerreyes, D.; Coulembier, O.; Sardon, H. Isomorphic Polyoxyalkylene Copolyethers Obtained by Copolymerization of Aliphatic Diols. *Macromolecules* **2019**, *52*, 3506−3515.
(36) Flores, I.; Demarteau, J.; Müller, A. J.; Etxeberria, A.; Irusta, L.; Bergman, F.; Koning, C.; Sardon, H. Screening of different organocatalysts for the sustainable synthesis of PET. *Eur. Polym. J.* **2018**, *104*, 170−176.
(37) Miran, M. S.; Kinoshita, H.; Yasuda, T.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties determined by ΔpKa for protic ionic liquids based on an organic super-strong base with various Brønsted acids. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5178−5186.
(38) Maton, C.; De Vos, N.; Stevens, C. V. Ionic liquid thermal stabilities: decomposition mechanisms and analysis tools. *Chem. Soc. Rev.* **2013**, *42*, 5963−5977.
(39) Cao, Y.; Mu, T. Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis. *Ind. Eng. Chem. Res.* **2014**, *53*, 8651−8664.
(40) Xue, Z.; Qin, L.; Jiang, J.; Mu, T.; Gao, G. Thermal, electrochemical and radiolytic stabilities of ionic liquids. *Phys. Chem. Chem. Phys.* **2018**, *20*, 8382−8402.
(41) Miran, M. S.; Hoque, M.; Yasuda, T.; Tsuzuki, S.; Ueno, K.; Watanabe, M. Key factor governing the physicochemical properties and extent of proton transfer in protic ionic liquids: ΔpKa or chemical structure? *Phys. Chem. Chem. Phys.* **2019**, *21*, 418−426.
(42) Chang, S.; Sheu, M.-F.; Chen, S.-M. Solid-state polymerization of poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **1983**, *28*, 3289−3300.
(43) Ma, Y.; Agarwal, U. S.; Sikkema, D. J.; Lemstra, P. J. Solid-state polymerization of PET: influence of nitrogen sweep and high vacuum. *Polymer* **2003**, *44*, 4085−4096.
(44) de Ilarduya, A. M.; Muñoz-Guerra, S. Chemical Structure and Microstructure of Poly(alkylene terephthalate)s, their Copolyesters, and their Blends as Studied by NMR. *Macromol. Chem. Phys.* **2014**, *215*, 2138−2160.
(45) Hariharan, R.; Pinkus, A. G. Useful NMR solvent mixture for polyesters: Trifluoroacetic acid-d/chloroform-d. *Polym. Bull.* **1993**, *30*, 91−95.
(46) Kenwright, A. M.; Peace, S. K.; Richards, R. W.; Bunn, A.; MacDonald, W. A. End group modification in poly(ethylene terephthalate. *Polymer* **1999**, *40*, 2035−2040.
(47) Farah, S.; Kunduru, K. R.; Basu, A.; Domb, A. J.8 - Molecular Weight Determination of Polyethylene Terephthalate. In *Poly(-Ethylene Terephthalate) Based Blends, Composites and Nanocomposites*; Visakh, P. M., Liang, M., Eds.; William Andrew Publishing: Oxford, 2015; pp 143−165.
(48) Chen, J.-W.; Chen, L.-W. The kinetics of diethylene glycol formation in the preparation of polyethylene terephthalate. *J. Polym. Sci. A Polym. Chem.* **1998**, *36*, 3073−3080.
(49) Chen, L.-W.; Chen, J.-W. Kinetics of diethylene glycol formation from bishydroxyethyl terephthalate with proton catalyst in the preparation of poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **2000**, *75*, 1221−1228.
(50) Chen, L.-W.; Chen, J.-W. Kinetics of diethylene glycol formation from bishydroxyethyl terephthalate with zinc catalyst in the preparation of poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **2000**, *75*, 1229−1234.
(51) Chen, J.-W.; Chen, L.-W. The kinetics of diethylene glycol formation from bis-hydroxyethyl terephthalate with antimony catalyst in the preparation of PET. *J. Polym. Sci. A Polym. Chem.* **1999**, *37*, 1797−1803.
(52) CIE 15: Technical Report: Colorimetry, 3rd ed., International Commision on Illumination, 2004.
(53) Wang, L.; Nelson, G. A.; Toland, J.; Holbrey, J. D. Glycolysis of PET Using 1,3-Dimethylimidazolium-2-Carboxylate as an Organocatalyst. *ACS Sustain. Chem. Eng.* **2020**, *8*, 13362−13368.
(54) Al-Sabagh, A. M.; Yehia, F. Z.; Eissa, A.-M. M. F.; Moustafa, M. E.; Eshaq, G.; Rabie, A.-R. M.; ElMetwally, A. E. Glycolysis of Poly(ethylene terephthalate) Catalyzed by the Lewis Base Ionic Liquid [Bmim][OAc]. *Ind. Eng. Chem. Res.* **2014**, *53*, 18443−18451.
(55) Martínez-Castañeda, Á.; Poladura, B.; Rodríguez-Solla, H.; Concellón, C.; del Amo, V. Direct Aldol Reactions Catalyzed by a Heterogeneous Guanidinium Salt/Proline System under Solvent-Free Conditions. *Org. Lett.* **2011**, *13*, 3032−3035.
(56) Baghbanian, S. M.; Tajbakhsh, M.; Farhang, M. Protic guanidinium ionic liquid as a green and highly efficient catalyst for the synthesis of functionalized spirochromenes under solvent-free conditions. *C. R. Chim.* **2014**, *17*, 1160−1164.
(57) Xu, J.; Liu, J.; Li, Z.; Wang, H.; Xu, S.; Guo, T.; Zhu, H.; Wei, F.; Zhu, Y.; Guo, K. Guanidinium as bifunctional organocatalyst for ring-opening polymerizations. *Polymer* **2018**, *154*, 17−26.
(58) Li, H.; Zhang, Q.; Huang, W.; Sheng, J.; Li, A.Method for Synthesizing Polylactide via Ring-Opening Polymerization. US20170009011A1, 2017.
(59) Gao, H.; Han, B.; Li, J.; Jiang, T.; Liu, Z.; Wu, W.; Chang, Y.; Zhang, J. Preparation of Room-Temperature Ionic Liquids by Neutralization of 1,1,3,3-Tetramethylguanidine with Acids and their Use as Media for Mannich Reaction. *Synth. Commun.* **2004**, *34*, 3083−3089.
(60) King, A. W. T.; Asikkala, J.; Mutikainen, I.; Järvi, P.; Kilpeläinen, I. Distillable Acid−Base Conjugate Ionic Liquids for Cellulose Dissolution and Processing. *Angew. Chem., Int. Ed.* **2011**, *50*, 6301−6305.
(61) Rauber, D.; Philippi, F.; Zapp, J.; Kickelbick, G.; Natter, H.; Hempelmann, R. Transport properties of protic and aprotic guanidinium ionic liquids. *RSC Adv.* **2018**, *8*, 41639−41650.
(62) Tolstikova, L. L.; Bel'skikh, A. V.; Shainyan, B. A. Trifluoromethanesulfonate, trifluromethylsulfonylimide, and bis-(trifluoromethylsulfonyl)imide salts and ionic liquids based on 1,8-diazabicyclo[5.4.0]undec-7-ene and 1,5-diazabicyclo[ 4.3.0]non-5-ene. *Russ. J. Org. Chem.* **2010**, *46*, 383−388.
(63) Sundermeyer, W.; Waldi, J. Synthese und Reaktionen Chinuclidin-stabilisierter Sulfene, R1R2C=SO2←N(CH2CH2)3CH. *Chem. Ber.* **1990**, *123*, 1687−1690.
(64) Antuganov, D.; Zykov, M.; Timofeev, V.; Timofeeva, K.; Antuganova, Y.; Orlovskaya, V.; Fedorova, O.; Krasikova, R. Copper-Mediated Radiofluorination of Aryl Pinacolboronate Esters: A Straightforward Protocol by Using Pyridinium Sulfonates. *Eur. J. Org.* **2019**, *2019*, 918−922.
(65) Messmore, B. W.; Hulvat, J. F.; Sone, E. D.; Stupp, S. I. Synthesis, Self-Assembly, and Characterization of Supramolecular Polymers from Electroactive Dendron Rodcoil Molecules. *J. Am. Chem. Soc.* **2004**, *126*, 14452−14458.
(66) Dinçalp, H.; Kızılok, Ş.; İçli, S. Fluorescent macromolecular perylene diimides containing pyrene or indole units in bay positions. *Dyes Pigm.* **2010**, *86*, 32−41.
(67) Govindarajan, S. R.; Jain, T.; Choi, J.-W.; Joy, A.; Isayeva, I.; Vorvolakos, K. A hydrophilic coumarin-based polyester for ambient-temperature initiator-free 3D printing: Chemistry, rheology and interface formation. *Polymer* **2018**, *152*, 9−17.
(68) Mohamed, S.; Tocher, D. A.; Vickers, M.; Karamertzanis, P. G.; Price, S. L. Salt or Cocrystal? A New Series of Crystal Structures Formed from Simple Pyridines and Carboxylic Acids. *Cryst. Growth Des.* **2009**, *9*, 2881−2889.


https://doi.org/10.1021/acs.macromol.2c01410
*Macromolecules* XXXX, XXX, XXX−XXX

(69) Wang, R.; Sun, M.; Jiang, H. Solvent-free tetrahydropyranylation of alcohols catalyzed by amine methanesulfonates. *Res. Chem. Intermed.* **2011**, *37*, 61−67.
(70) Jeong, Y.; Kim, D.-Y.; Choi, Y.; Ryu, J.-S. Intramolecular hydroalkoxylation in Brønsted acidic ionic liquids and its application to the synthesis of (±)-centrolobine. *Org. Biomol. Chem.* **2011**, *9*, 374−378.
(71) Zhu, X.; Wang, Y.; Li, H. Do all the protic ionic liquids exist as molecular aggregates in the gas phase? *Phys. Chem. Chem. Phys.* **2011**, *13*, 17445−17448.
(72) Chen, H.; Jia, L.; Xu, X.; Mao, J.; Wang, Y.; Wang, C.; Li, H. Electronic effect of ionic-pair substituents. *J. Phys. Org. Chem.* **2013**, *26*, 460−466.
(73) Tong, X.; Ma, Y.; Li, Y. An efficient catalytic dehydration of fructose and sucrose to 5-hydroxymethylfurfural with protic ionic liquids. *Carbohydr. Res.* **2010**, *345*, 1698−1701.
(74) Tong, X.; Li, Y. Efficient and Selective Dehydration of Fructose to 5-Hydroxymethylfurfural Catalyzed by Brønsted-Acidic Ionic Liquids. *ChemSusChem* **2010**, *3*, 350−355.
(75) Prasad, V.; Kale, R. R.; Mishra, B. B.; Kumar, D.; Tiwari, V. K. Diacetoxyiodobenzene Mediated One-Pot Synthesis of Diverse Carboxamides from Aldehydes. *Org. Lett.* **2012**, *14*, 2936−2939.
(76) Biyikal, M.; Löhnwitz, K.; Meyer, N.; Dochnahl, M.; Roesky, P. W.; Blechert, S. *β*-Diketiminate Zinc Complexes for the Hydroamination of Alkynes. *Eur. J. Inorg. Chem.* **2010**, *2010*, 1070−1081.
(77) Wu, G.; Wang, X.; Liu, H. Highly Efficient One-Pot Synthesis of 2,4-Disubstituted Thiazoles Using Au(I) Catalyzed Oxidation System at Room Temperature. *Catalysts* **2016**, *6*, 126.





https://doi.org/10.1021/acs.macromol.2c01410
*Macromolecules* XXXX, XXX, XXX−XXX