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RESEARCH ARTICLE

Organocatalytic depolymerization of poly(trimethylene carbonate)

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Abstract

Aliphatic polycarbonates have attracted attention as degradable and sustainable materials contributing to the circular plastic economy. Their chemical recycling has not been sufficiently studied. In this study, the efficacy of organocatalysts for depolymerization of poly(trimethylene carbonate) (PTMC), a representative aliphatic polycarbonate, is investigated using several organic acids and bases. The hydrolysis of PTMC produces the water-soluble degradates propane-1,3-diol (PD) and CO₂. A phosphazene base P₂-*t*-Bu shows high activity for the hydrolysis, yielding up to 31% and 89% of PD in the homogeneous reaction at around 27°C and the inhomogeneous reaction under the reflux condition, respectively. By contrast, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) exhibits exceptionally high catalytic activity for the methanolysis of PTMC, producing PD and dimethyl carbonate. This is because of dual hydrogen-bonding activation, which completes the inhomogeneous reaction in a few hours at around 27°C while yielding more than 90% of PD. The reaction rate of the TBD-catalyzed methanolysis depends on the concentration of the nucleophile and catalyst, and the ratio of the nucleophile to the substrate affects the PD yield. These results provide a highly promising standard for chemical recycling of functionalized aliphatic polycarbonates that could potentially be applied to sustainable materials in the future.

KEYWORDS

aliphatic polycarbonates, depolymerization, hydrolysis, methanolysis, organocatalysts

1 | INTRODUCTION

Polycarbonates are widely used in many fields ranging from electronics to medical devices.^{1–3} Bisphenol-A polycarbonate (BPA-PC) is the most common polycarbonate used as organic glass in applications requiring transparency, thermal stability, and impact resistance. Along with poly(ethylene terephthalate) (PET), BPA-PC has recently

drawn attention as a recyclable and upcyclable polymer.^{2,4,5} Poly(trimethylene carbonate) (PTMC), a representative aliphatic polycarbonate, has been clinically applied in sutures and drug delivery owing to its biodegradability and absorbability.^{3,6} Recent progress in catalysis has enabled more accessible PTMC production and increasing development of PTMC analogs with functional side chains for applications in biomedical

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devices.^{7,8} Polycarbonates are recognized as sustainable polymers derived from CO₂,^{9,10} and thus PTMC analogs and the similar aliphatic polycarbonates are expected to be effective countermeasures to tackle the recent plastic-related problems as degradable and sustainable polymers. Aliphatic polycarbonates with rigid and bulky side chains that exhibit high thermal properties have been developed.^{11,12} These are promising alternatives to conventional petroleum-based polymers.

Considering the possible increase in demands for PTMC analogs and related aliphatic polycarbonates, there is a significant need to investigate the depolymerization properties of a simple aliphatic polycarbonate such as PTMC. However, the depolymerization properties of aliphatic polycarbonates have not been sufficiently studied from the viewpoint of chemical recycling. Biodegradability of aliphatic polycarbonates in natural and aqueous environments, including the ocean, is not high compared to aliphatic polyesters.¹³ This is owing to the stability of their carbonate group.¹³ In vitro hydrolytic properties of PTMC have been studied under different pH conditions and in the presence of enzymes, indicating gradual decreases in molecular weight and mass over days to weeks under mild conditions.^{14,15} On-demand and prompt degradation via chemical processes should also be considered for recyclable and sustainable applications.^{1,9} Thus, catalytic depolymerization could play a more significant role in the recycling and upcycling of PTMC analogs, as has been explored for BPA-PC and PET.^{2,4,5,16,17} These catalytic depolymerizations occur in a shorter time range (~hours) than in vivo degradation and enzymatic degradation (~days and weeks).

The scope of organocatalytic transesterifications has expanded in the last two decades to not only ring-opening

polymerization but also depolymerization of polyesters and polycarbonates,^{18–20} leading to the further development of new catalyst systems.²¹ Aromatic polyesters and polycarbonates have been studied as the primary target materials for organocatalytic depolymerization^{22,23} because of the potential impact and utility of chemical recycling of these polymers used in commodities and industrial products. The chemical and physical stabilities of these polymers often require harsh conditions for chemical degradation, e.g., heating at high temperatures.^{24–26} Aliphatic polycarbonates have been out of the scope for the catalytic depolymerization. However, as described above, now it is significant to establish an efficient depolymerization process of aliphatic polycarbonates for their future applications in sustainable and recyclable materials. PTMC and non-substituted aliphatic polycarbonates have lower thermal properties and more options for degradation media because of their better solubility and compatibility compared to aromatic polyesters and polycarbonates. Thus, the chemical recycling of these aliphatic polycarbonates can be achieved in a more energy-efficient and greener manner with the aid of an appropriate potent catalyst. In this context, we have addressed the organocatalytic depolymerization of PTMC as a standard model using several organic acids and bases to elucidate its degradation behavior in the presence of different media and catalysts (Figure 1).

2 | EXPERIMENTAL

2.1 | Materials

PTMC, 1-*tert*-butyl-2,2,4,4,4-pentakis-(dimethylamino)-2Λ⁵,4Λ⁵-catenadi(phosphazene) (P₂-*t*-Bu) solution (2 M in

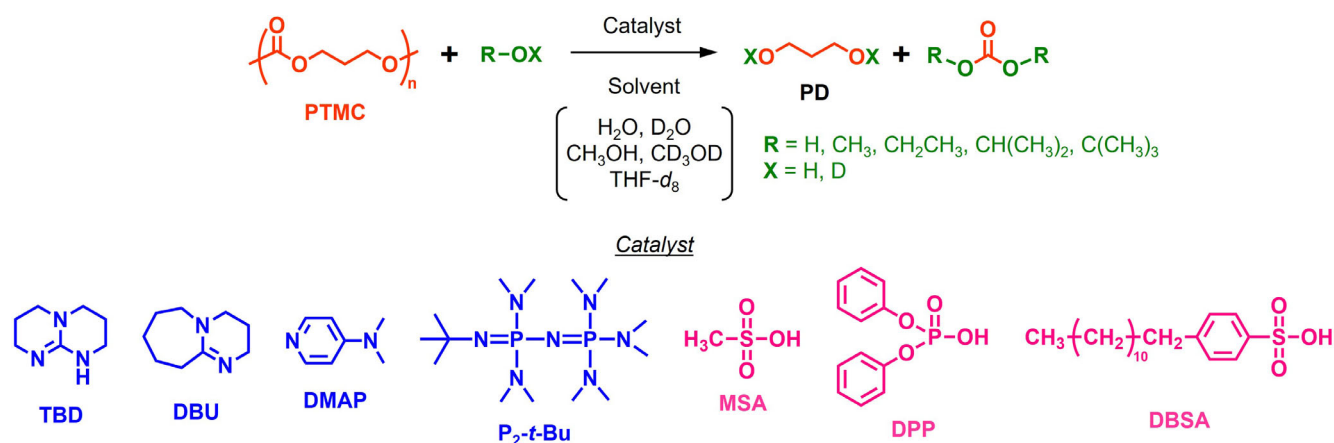


FIGURE 1 Depolymerization of PTMC in solution using different organocatalysts. PD: Propane-1,3-diol; TBD: 1,5,7-Triazabicyclo[4.4.0]dec-5-ene; DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene; DMAP: *N,N*-Dimethylaminopyridine; P₂-*t*-Bu: 1-*tert*-Butyl-2,2,4,4,4-pentakis-(dimethylamino)-2Λ⁵,4Λ⁵-catenadi(phosphazene); MSA: Methanesulfonic acid; DPP: Diphenyl phosphate; DBSA: Dodecylbenzenesulfonic acid.

tetrahydrofuran [THF]), and methanesulfonic acid (MSA) were purchased from Sigma-Aldrich Japan (Tokyo, Japan). 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *N,N*-dimethylaminopyridine (DMAP), diphenyl phosphate (DPP), and dodecylbenzenesulfonic acid (DBSA) were purchased from Tokyo Chemical Industry (TCI; Tokyo, Japan). Deuterated solvents were purchased from Kanto Chemical (Tokyo, Japan). All chemicals were used as received.

2.2 | Measurements

^1H and ^{13}C NMR spectra were measured on a JEOL JNM-ECX400 spectrometer operated at 400 and 100 MHz, respectively. Tetramethylsilane (TMS) and residual solvent peaks were used as references for the calibration of the chemical shifts. Molecular weights and distributions were determined by size-exclusion chromatography (SEC) at 40°C in THF using an HLC-8420 EcoSEC Elite (Tosoh, Tokyo, Japan) with a built-in refractive index and UV detectors, a column oven, and two serially connected TSK-gel columns (SuperMultiporeHZ-M). Polystyrene (PS) standards with M_n ranging from 5.9×10^2 to 7.1×10^5 g mol $^{-1}$ were used for the calibration of the molecular weights. The electrostatic charges of the reagents were estimated by Spartan'18 (Wavefunction, Tokyo, Japan).

2.3 | Degradation test

2.3.1 | Hydrolysis

General procedure in inhomogeneous solution

PTMC was cut into small pieces with ~2 mm on a side (Figure S1a). In a 2 ml-vial, PTMC (10 mg; 0.1 mmol as a monomer repeating unit) was placed and mixed with a solution of a catalyst (0.05 mmol) in D₂O (1.0 ml, 55 mmol). The mixture was stirred at 40°C, and the supernatant was used to confirm the content and structure of the water-soluble degradates using ^1H NMR. After carrying out the reaction for a predetermined time, basic and acidic catalysts were quenched by trifluoroacetic acid (TFA) and pyridine, respectively. The residual PTMC was dried in a vacuum and dissolved in THF for SEC measurements to confirm the change in the molecular weight.

For a reflux condition, PTMC (100 mg; 1.0 mmol as a monomer repeating unit) was mixed with a solution of a catalyst (0.5 mmol) in D₂O (5.0 ml) in a 30 ml-Schlenck tube equipped with a reflux condenser. The mixture was stirred and heated by an aluminum block for 12 h at

120°C (solution temperature: ~100°C). The supernatant and the residual PTMC were treated and characterized the same as above.

General procedure in homogeneous solution

PTMC (10 mg; 0.1 mmol as a monomer repeating unit) was dissolved in deuterated THF (THF-*d*₈; 1.0 ml). A solution of a catalyst (0.01 mmol) in D₂O (29 μl, 1.6 mmol) was then added to the polymer solution. The mixed solution was stirred at around 27°C and directly used for ^1H NMR measurements to monitor the progress of the reaction.

2.3.2 | Methanolysis

General procedure in inhomogeneous solution

PTMC (10 mg; 0.1 mmol as a monomer repeating unit) was placed in a 2 ml-vial and mixed with a solution of a catalyst (0.01 mmol) in deuterated methanol (CD₃OD; 1.0 ml, 24.6 mmol) containing 0.03 wt% of TMS as the internal standard. The mixture was then stirred at around 27°C. ^1H NMR spectra of the supernatant at different time points were analyzed to trace the progress of the reaction by observing the signals of the eluted degradates. The catalysts were quenched as described above. After the supernatant was removed, the residual PTMC was dried in a vacuum and dissolved in THF for SEC measurements to confirm the change in the molecular weight.

General procedure in homogeneous solution

PTMC (10 mg; 0.1 mmol as a monomer repeating unit) was dissolved in THF-*d*₈ (1.0 ml) containing a catalyst (0.01 mmol). CD₃OD (65 μl, 1.6 mmol) was then added to the polymer solution. The mixed solution was stirred at around 27°C and directly analyzed using ^1H NMR to monitor the progress of the reaction.

2.3.3 | Alcoholysis

General procedure in inhomogeneous alcoholysis

PTMC (100 mg; 1.0 mmol as a monomer repeating unit) was placed in a 2 ml-vial and mixed with a solution of TBD (14 mg, 0.1 mmol) in an alcohol (1.0 ml). The mixture was then stirred at around 20°C. After a predetermined time, TFA was added for the termination. The alcohol as the reaction solvent was evaporated and dried at reduced pressure, and the residue was dissolved in THF and THF-*d*₈ for SEC and ^1H NMR characterizations.

3 | RESULTS AND DISCUSSION

3.1 | Inhomogeneous hydrolysis

Unlike aliphatic polyesters, PTMC is known to tolerate hydrolysis in a broad pH range. This stability is explained by the conjugate structure of the carbonate bond, which is more stable than the ester group.¹³ Acidic and alkaline hydrolysis of esters is driven by the protonation of carbonyl oxygens and the nucleophilic attack by the hydroxide anion on the carbonyl carbons. Organocatalysts play a similar role in polymerization and depolymerization: organoacids activate carbonyl groups and organobases enhance the nucleophilicity of nucleophiles through hydrogen bonding.¹⁸ TBD has exhibited exceptional catalytic activity owing to its dual hydrogen bonding mechanism in the depolymerization of BPA-PC and PET, which usually proceeds in inhomogeneous systems.^{22–24} Thus, we expect that TBD may efficiently promote the hydrolytic depolymerization of PTMC. DBU,²⁴ P₂-*t*-Bu,²⁷ MSA,²⁸ and DBSA were also evaluated as comparable examples. Hydrolysis of PTMC generates propane-1,3-diol (PD) and CO₂, which forms an adduct with nitrogen bases to mitigate the catalytic activity. Although the acid–base complexes of TBD and DBU are known to retain high catalytic activity,^{21,24} the catalytic loading was set to 0.5 equivalents relative to the repeating unit of PTMC. The rate of inhomogeneous reaction depends on the surface area of the substrate. Thus, we used small pieces of PTMC cut into approximately 2³ mm³ for greater contact with the reaction media containing a catalyst.

Consequently, no catalyst was able to complete the inhomogeneous hydrolysis of PTMC in D₂O with gentle heating at 40°C. The polymers persisted after 20-day reactions in all the cases. NMR studies of the D₂O supernatants reveal that small amounts of PTMC are degraded, as small signals corresponding to PD are found at 3.66 and 1.77 ppm (Figure S2a). The amount of PD eluted in the supernatant (= [PD]) was estimated from the integral ratios of PD to those of catalysts, which had an initial concentration of 0.05 M. The time course of PD production (= [PD]/[PTMC]₀; [PTMC]₀ = 0.1 M) indicates a gradual increase of PD over 20 d (500 h), which does not reach a plateau for any of the reactions (Figure 2A). P₂-*t*-Bu, DBU, and DBSA are more active than TBD for the inhomogeneous hydrolysis of PTMC, while MSA is less active. Except for DBSA, the decreases in molecular weight of the residual PTMC are consistent with the production of PD (Figure 2B). The SEC traces of PTMC treated with TBD and MSA in D₂O are almost identical to that of the original (*M*_n 4.5 × 10⁴ g mol⁻¹, Đ 1.76), while those of PTMC treated with P₂-*t*-Bu, DBU, and DBSA

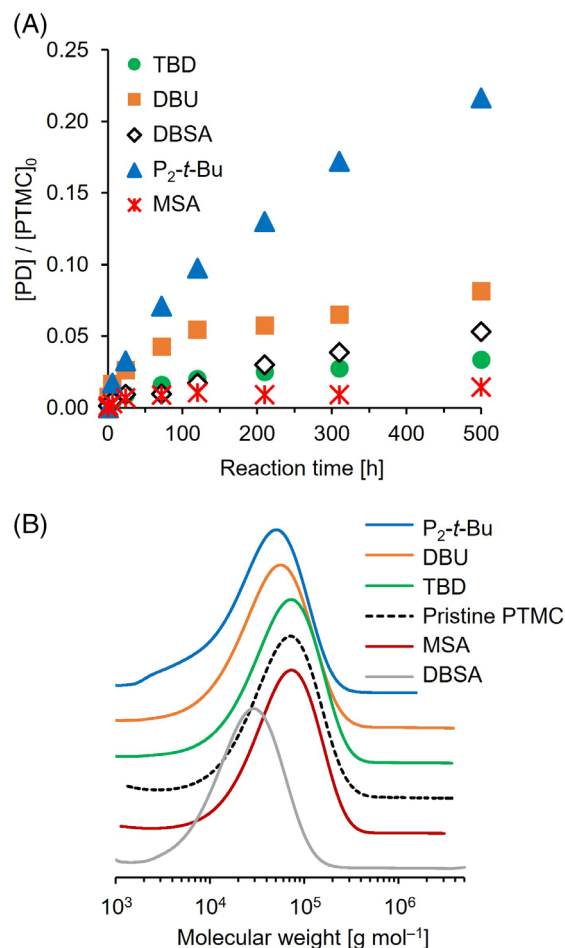


FIGURE 2 Time courses of PD production during the inhomogeneous hydrolysis of PTMC in the presence of different organocatalysts (0.05 M; 0.5 equiv. relative to the repeating unit of PTMC) performed at 40°C (A); SEC traces of the residual PTMC at each reaction (THF, 40°C). The molecular weights were calibrated by polystyrene standards (B).

shift to lower molecular weights. In addition, the SEC trace for P₂-*t*-Bu contains a low-molecular-weight shoulder below 10⁴ g mol⁻¹ (Figure 2B). These molecular weight decreases are believed to result from surface erosion-type degradation, in which PTMC chains are randomly cleaved. Since PTMC is an amorphous polymer, the end groups are not localized differently from semi-crystalline polymers. Thus, carbonate bonds nonspecifically undergo the attack of the nucleophile at the interface with the reaction media.

These results demonstrate that P₂-*t*-Bu and DBU are more efficient catalysts than TBD in the hydrolysis of PTMC and suggest that catalytic activity is not directly associated with their respective acidity and basicity. The p*K*_a values in acetonitrile as a parameter of the basicity are 24.3, 26, and 33.5 for DBU, TBD, and P₂-*t*-Bu, respectively.^{24,29,30} The low catalytic activity of TBD known as a

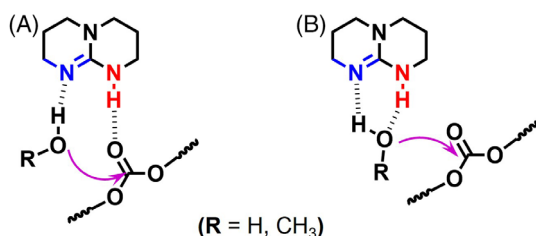


FIGURE 3 Bifunctionality of TBD. H-bond acceptor ($-\text{N}=\text{}$) enhances the nucleophilicity of the hydroxy group, while H-bond donor ($-\text{NH}$) activates the carbonyl group in the PTMC main chain (A); H-bond donor ($-\text{NH}$) may mitigate the nucleophilicity of the hydroxy group (B).

bifunctional catalyst³¹ may be explained by the presence of dual hydrogen bonds (H-bonds) consisting of the sp^2 nitrogen ($-\text{N}=\text{}$) as an H-bond acceptor and the hydrogen of the secondary amine ($-\text{NH}$) as an H-bond donor. The efficient catalysis of TBD is explained by the dual H-bond activation of a nucleophile ($\text{R}-\text{OH}$) and a substrate (carbonate) (Figure 3A). However, the dual H-bonds may also be served to bind to the hydroxy group of $\text{R}-\text{OH}$, thus mitigating the nucleophilicity of the oxygen atom by hydrogen bonding with NH of TBD (Figure 3B). The latter becomes dominant in the hydrolysis as the case for $\text{R}=\text{H}$ in Figure 3. Water may interfere in the interaction between TBD and PTMC. CO_2 as the degradate in the hydrolysis of PTMC may form an adduct with basic catalysts to mitigate the catalytic activity. However, CO_2 is not most likely the reason for the low efficiency of TBD because DBU and $\text{P}_2\text{-}t\text{-Bu}$ are also subjected to the same. Nonetheless, the generation of PD was low ($<10\%$ relative to the repeating unit in PTMC initially loaded) during these catalytic hydrolyses of PTMC. Except for the case of hydrolysis catalyzed by $\text{P}_2\text{-}t\text{-Bu}$, these results are similar to those of previous studies regarding the alkaline degradation of PTMC.¹⁴ DBSA exhibits a different catalytic behavior since it leads to a lower production of PD (Figure 2A), while yielding the lowest molecular weight of the residual PTMC (Figure 2B). This specificity is possibly because of the surfactant properties of DBSA, which facilitate the infiltration of water inside PTMC.

Furthermore, a higher-temperature condition was examined for the hydrolysis of PTMC using selected catalysts: TBD, DBU, and $\text{P}_2\text{-}t\text{-Bu}$. The inhomogeneous mixture of PTMC and D_2O was refluxed in the presence of catalysts for 12 h. A noticeable decrease in the volume of the PTMC pieces was observed, which also reflected the signal intensities of PD in the supernatants of the ^1H NMR spectra (Figure S2b). The soluble degradates in D_2O were found to comprise predominantly PD and catalysts (Figure S2b). The weight changes of PTMC after the reaction, which are recognized as a percentage of the

degradation, were 20%, 89%, and 91% for the catalysis by TBD, $\text{P}_2\text{-}t\text{-Bu}$, and DBU, respectively (Figure S3). The trend of catalytic activity appears similar to that for the hydrolysis performed at 40°C . Most of the PTMC pieces disappeared in the first 1 h in the $\text{P}_2\text{-}t\text{-Bu}$ -catalyzed hydrolysis, whereas DBU-catalyzed hydrolysis required more than 6 h to diminish the pieces. The SEC traces of the residual PTMC suggest that all refluxed hydrolysis significantly promotes the degradation of PTMC (Figure S4a). The residual PTMC at the DBU-catalyzed hydrolysis shows a significant decrease in molecular weight. Due to the high temperature, water appears to infiltrate PTMC more interiorly than that in hydrolysis at 40°C , resulting in bulk erosion-type degradation. The residue in the DBU-catalyzed hydrolysis was further characterized by a matrix-assisted laser deposition ionization time-of-flight (MALDI-TOF) mass spectroscopy, proving the presence of low molecular weight PTMC with deuterated end groups as a result of an attack by D_2O (Figure S4b).

3.2 | Homogeneous hydrolysis

Homogeneous solution reactions are more appropriate for elucidating reaction details at the molecular level. Deuterated THF was used for the NMR studies of homogeneous hydrolysis of PTMC owing to the solubility of PTMC and its miscibility with water. In addition to TBD, we examined $\text{P}_2\text{-}t\text{-Bu}$ and DBU, which show high catalytic activity in the inhomogeneous hydrolysis of PTMC discussed in the previous section. Excess loading of nucleophiles facilitates the transesterification-based depolymerization, as observed in the alcoholysis of PET and BPA-PC.^{21–24} Thus, we added 16 equivalents of D_2O as a nucleophile with 0.1 equivalents of catalysts relative to the repeating unit of PTMC for the homogeneous depolymerization in $\text{THF-}d_8$ at around 27°C . The reactions were monitored by ^1H NMR for 11 d. The characteristic signals of PTMC are observed as the major component in all reaction solutions after 11 d (Figure S5). In addition, signals corresponding to PD and oligomers generated by the hydrolysis are confirmed in the reaction mixture treated by TBD and $\text{P}_2\text{-}t\text{-Bu}$. Compared to its use in inhomogeneous hydrolysis, DBU did not exhibit much potency when used in homogeneous hydrolysis. Three structure parts corresponding to the CH_2 of PTMC, hydroxy end, and PD (Figure 4A) are identified from the signals at 1.98, 1.78, and 1.63 ppm, respectively, in the ^1H NMR spectra (signals b, c, and f in Figure S5). The composition of these three structures is determined from the integral ratios of the signals (I_b , I_c , and I_f) in the ^1H NMR spectra.

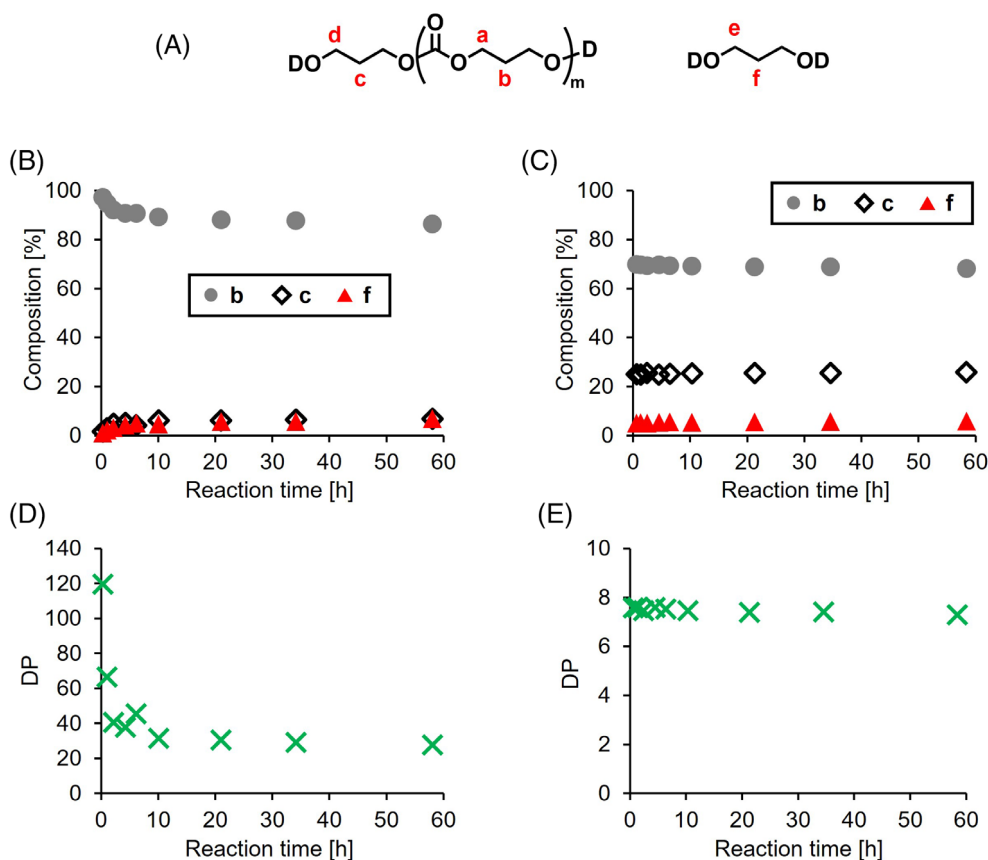


FIGURE 4 Results of homogeneous hydrolysis of PTMC. Assignments of protons for the hydrolysates of PTMC in ¹H NMR (A); time courses of the composition of each structure in the reaction mixture treated by TBD (B) and P₂-t-Bu (C); degrees of polymerization (DPs) of the partially hydrolyzed PTMC in the reaction mixture treated by TBD (D) and P₂-t-Bu (E). The composition of b was calculated by $I_b / (I_b + I_c + I_f) \times 100$ (%), where I_x denotes the integral ratio of the signal x in ¹H NMR. The compositions of c and f were derived similarly. DPs were calculated by $(I_b + I_c) / I_c \times 2$.

While the composition remains nearly unchanged in the reaction using P₂-t-Bu (Figure 4B), a composition change is observed in the reaction mixture of the TBD-catalyzed hydrolysis during the first 10 h (Figure 4C). The compositions of PD are almost the same for the reactions using TBD and P₂-t-Bu (7% and 6% at 60 h). A higher amount of the end unit (signal c) is observed in the reaction mixture treated by P₂-t-Bu than in that treated by TBD (Figure 4B, C). These results indicate that shorter lengths of oligomers are produced as the PTMC hydrolysates are formed during the reaction using P₂-t-Bu. This is supported by the degrees of polymerization (DPs) of the partially hydrolyzed PTMC (Figure 4D, E). We assumed that the chain scission of PTMC by hydrolysis occurs randomly and that hydroxy ends are formed at both ends of the oligomers (Figure 5). Thus, the DPs were calculated from the integral ratios of signals b and c, and given as $(I_b + I_c) / I_c \times 2$.

No catalysts fully depolymerized PTMC via hydrolysis to yield PD in the homogeneous system at room temperature (~27°C). The reactions appear to reach a plateau at a very early stage (Figure 4B, C). The compositions of signal b at 10 h are 89% and 69% for the reaction using TBD and P₂-t-Bu, respectively. This indicates that 11% and 31% of carbonate bonds are cleaved to generate CO₂ when using TBD and P₂-t-Bu, respectively. The

organobasic catalysts are loaded at 10% relative to PTMC in the homogeneous hydrolysis, and thus are not significantly affected by the generated CO₂. This study reveals that TBD and P₂-t-Bu facilitate the homogeneous hydrolysis of PTMC in THF to produce short-length PTMC oligomers. The difference in the catalytic activities between TBD and P₂-t-Bu is most likely attributed to their basicity; the hydrolysis by P₂-t-Bu provides shorter oligomers faster. P₂-t-Bu has enough basicity to serve as an anionic polymerization catalyst.³² The solvation and polarity of the media may correlate with the inverted activity of TBD and DBU between homogeneous and inhomogeneous hydrolysis. Consequently, the strong basicity of P₂-t-Bu is necessary to activate water as the nucleophile for the hydrolysis of PTMC in the inhomogeneous and homogeneous systems.

3.3 | Inhomogeneous methanolysis

Alcoholysis is often employed as an alternative method to hydrolysis for the depolymerization of polyesters and polycarbonates.^{21–25} Besides diols, other degradates are recovered in the forms of esters and carbonates (Figure 5) for direct usage in transesterification-based repolymerization,²¹ which is advantageous in chemical recycling. In addition,

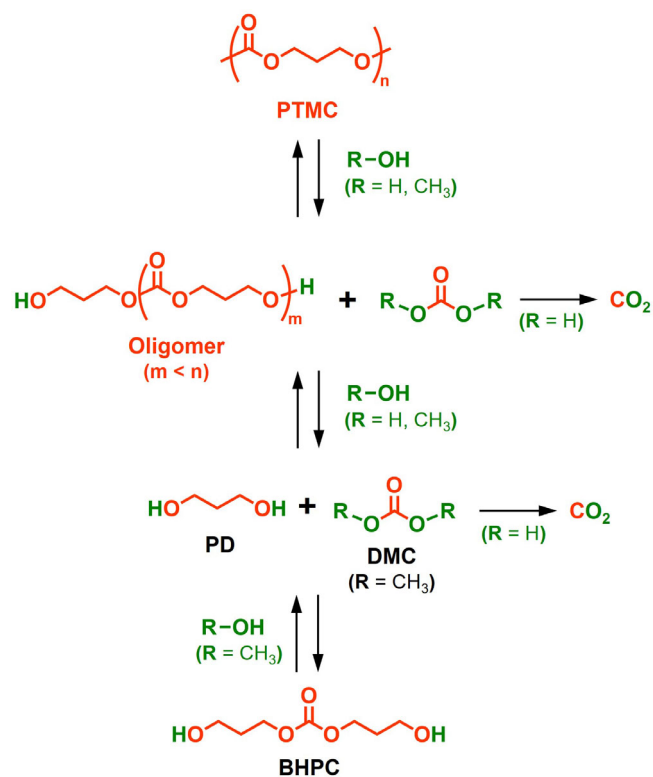


FIGURE 5 Schematic representation of the depolymerization of PTMC by hydrolysis ($R = H$) and methanolysis ($R = CH_3$). All the steps are equilibrium reactions. DMC: Dimethyl carbonate; BHPC: Bis(3-hydroxypropyl) carbonate.

the growing production of short-chain alcohols from renewable resources, such as biomass and CO_2 ,^{33–35} may facilitate alcoholysis as a principal degradation approach. We employed deuterated methanol as a nucleophile and degradation medium in this study to simplify the identification of soluble degradates in the medium using 1H NMR. PTMC is insoluble in methanol, and thus the depolymerization proceeds inhomogeneously. As with the depolymerization of PET, the completion of the reaction was confirmed by visual inspection of the disappearance of PTMC as the solution became clear. We examined several catalysts and conditions for the inhomogeneous methanolysis of PTMC. The results are summarized in Table 1.

The depolymerization appeared to be complete at 36 h in the presence of TBD (0.01 mmol; run 1 in Table 1). Like the case of inhomogeneous hydrolysis, the amount of the produced PD and oligomers were calculated based on the integral ratio of the catalysts dissolved in the supernatants at a predetermined concentration using the 1H NMR spectra (Figure S6). The percentages of degradation were calculated from the percentage of the sum of the degradates out of PTMC initially loaded. The amount of the produced PD in the supernatant of

the TBD-catalyzed methanolysis (run 1 in Table 1) is highly comparable to the amount of PTMC initially loaded (~ 10 mg). Although no other catalysts complete the methanolysis of PTMC at the same time points (~ 40 h), the methanolysis carried out using DBU and P_2-t-Bu successfully produces PD dissolved in CD_3OD (Figure S6a). Based on the percentage of degradation, DBU promotes the methanolysis of PTMC more efficiently than P_2-t-Bu (runs 2 and 3 in Table 1), which is also confirmed by the SEC traces of the residual PTMC (Figure 6A). It should be noted that the pristine PTMC contains a small amount of low-molecular-weight fractions, which are degraded in the above three catalytic conditions. The peak shape in the SEC trace remains almost intact for the residual PTMC treated with P_2-t-Bu , while that for the DBU-catalyzed reaction broadens. Inhomogeneous methanolysis of PTMC with other catalysts, including DMAP, MSA, DPP, and DBSA, produces oligomers as the main product rather than PD (Figure S6b), and the amounts are small (runs 4–7 in Table 1). Other catalysts are significantly less active than TBD for methanolysis of PTMC. These results are consistent with the previous results for the alcoholysis of PET by mono-alcohols, in which TBD was found to be more active than the other catalysts, including DBU.²⁴ Considering that P_2-t-Bu is more basic than TBD, the dual H-bond activation mechanism (Figure 3A) is likely to be the reason for the higher activity of TBD. Successful catalysis of TBD depends on whether NH of TBD could participate in the interaction with the carbonyl groups of PTMC to accomplish the dual activation. Therefore, unlike water, methanol seems to be favorable to the dual activation, which may explain the significant difference in the catalytic activity of TBD between hydrolysis and methanolysis.

We further investigated the catalytic activity of TBD under different conditions. Depolymerization time decreased nearly by half when double the amount of TBD was used (0.02 mmol; run 8 in Table 1). Then, we increased the initial loading of both PTMC (100 mg) and TBD (0.1 mmol) by 10 times, while maintaining the volume of the medium at 1 ml and a 0.1 molar ratio of TBD to the repeating monomer unit of PTMC (run 9 in Table 1). After these changes, the depolymerization completed in a few hours, indicating that the degradation rate depends on the catalytic concentration for the inhomogeneous reaction. Furthermore, when double the amount of PTMC (200 mg) was loaded, the depolymerization time did not significantly change, as depolymerization occurred in 3 h (run 10 in Table 1). After the first cycle of the depolymerization, there are remaining amounts of unreacted methanol and TBD. Thus, we added PTMC (200 mg) to the reaction mixture of run 10 in Table 1.

Run ^a	PTMC (mg)	Catalyst	(mmol)	Time (h)	Degradation ^b (%)
1	10	TBD	0.01	36	>99
2	10	DBU	0.01	40	17
3	10	P ₂ - <i>t</i> -Bu	0.01	40	9.5
4	10	DMAP	0.01	40	1.4
5	10	MSA	0.01	40	1.4
6	10	DPP	0.01	40	1.4
7	10	DBSA	0.01	40	1.6
8	10	TBD	0.02	18	>99
9	100	TBD	0.1	2.5	>99
10	200	TBD	0.1	3	>99

TABLE 1 Inhomogeneous depolymerization of PTMC in deuterated methanol using different catalysts.

^aSmall pieces of PTMC (~2³ mm³) were placed in 1 ml of CD₃OD dissolving catalysts at around 27°C.

^bDetermined by ¹H NMR of the supernatant.

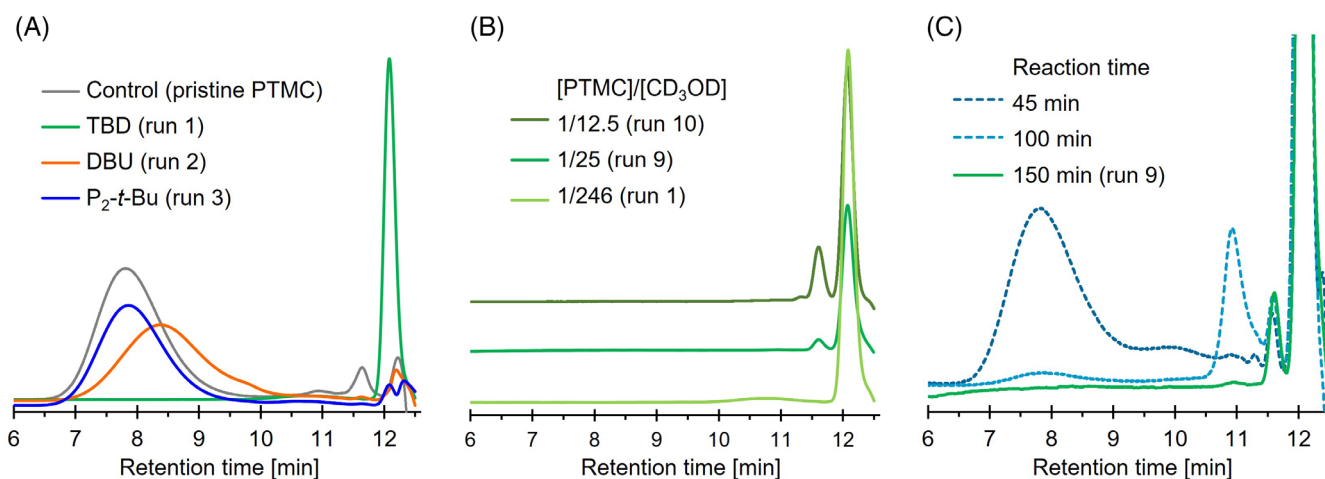


FIGURE 6 SEC traces (THF, 40°C) of the residues (A), soluble degradates in CD₃OD (B), and reaction mixtures (C) at the inhomogeneous methanolysis of PTMC. Molecular weights were calibrated by polystyrene standards.

The depolymerization required a slightly longer time for completion in comparison to the first cycle (~4 h). The third cycle required a much longer reaction time (>several days). This result is attributed to the increased concentrations of dimethyl carbonate (DMC) and PD as the degradates, which compete with the major reaction between PTMC and methanol (Figure 5). Thus, the reaction rate depends on the ratio of the nucleophile to the substrate. The molar ratios of CD₃OD to PTMC (as a repeating unit) are 25 and 12.5 for runs 9 and 10, respectively. Since these transesterification-based reactions are equilibrium reactions, as shown in Figure 5, the substrate to nucleophile ratio affects the composition of the products. In the glycolysis of PET, more than 8–16 equivalents of ethylene glycol are desirable for producing the monomer bis(hydroxyethyl) terephthalate with a negligible amount of oligomers.²² The ¹H and ¹³C NMR spectra of the reaction solution of run 10 in Table 1 (Figures S7 and

S8) were used to identify bis(3-hydroxypropyl)carbonate (BHPC) as the main byproduct in the methanolysis of PTMC with PD and DMC (Figure 5). The composition of BHPC increases in the degradation product as the ratio of PTMC to CD₃OD increases, as confirmed by the ¹H NMR spectra (Figure S7) and SEC traces of the reaction mixtures (Figure 6B). The elution time of BHPC appears to be approximately 11.7 min. The methanolysis product of run 10 in Table 1, showing two peaks in the SEC traces (Figure 6b), was then separated by recycling preparative high-pressure liquid chromatography. The major component (Fr1 in Figure S9a) was successfully isolated and identified as PD (Figures S9b and S9c).

The mechanistic insight of the degradation for the inhomogeneous methanolysis is also explained by surface erosion and random scission. The SEC traces of the reaction mixtures reflect the average information of molecular weights of the interior part of PTMC not degraded,

TABLE 2 Inhomogeneous depolymerization of PTMC catalyzed by TBD in different alcohols.

Run ^a	PTMC (mg)	TBD (mmol)	Alcohol	(ml)	Time (h)	Degradation ^b (%)
1	1000	1.0	Methanol (−0.55) ^c	10	36	>99
2	100	0.1	Methanol (−0.55) ^c	1	28	>99
3	100	0.1	CD ₃ OD (−0.57) ^c	1	4	>99
4	100	0.1	Ethanol (−0.59) ^c	1	24	>99
5	100	0.1	2-Propanol (−0.64) ^c	1	168	97
6	100	0.1	<i>t</i> -Butanol (−0.69) ^c	1	192	7.4

^aThe reaction was performed at around 20°C. Small pieces (~2³ mm³) of PTMC were used for runs 2–6.

^bDetermined by ¹H NMR.

^cThe values in parenthesis are electrostatic charge values of the oxygen atom on the hydroxy group, calculated by density functional theory.

the outer part of PTMC contacting with methanol to be degraded, and the degradates. In the middle of the reaction, the SEC traces of the reaction mixtures show high-molecular-weight and low-molecular-weight fractions, corresponding to pristine PTMC and PD and oligomers (Figure 6C). These results suggest that the degradation proceeds promptly and randomly at the interface, thus yielding little middle-molecular-weight fractions.

Subsequently, we demonstrated a larger-scale methanolysis of PTMC at around 20°C using a 1-gram chunk (Figure S1b and S1c) with the same stoichiometry as run 9 in Table 1 (PTMC/methanol = 0.1 g/ml, PTMC/TBD = 1/0.1 in the molar ratio). The chunk successfully disappeared to yield a homogeneous transparent solution after 36 h (run 1 in Table 2), indicating that the TBD-catalyzed inhomogeneous methanolysis is practicable, irrespective of the reaction scale and dimension of PTMC. The methanolysis using small pieces of PTMC was completed in 28 h (run 2 in Table 2), proving the advantage of greater surface area by the small pieces. These reaction times are significantly longer than that of the methanolysis at run 9 in Table 1 using CD₃OD. Then we found that the reactivity of CD₃OD is substantially higher than that of methanol (run 3 in Table 2; 4 h). The effects of the reaction temperature on the reaction rate are minor in the comparison between run 3 in Table 2 (4 h at 20°C) and run 9 in Table 1 (2.5 h at 27°C). A similar manner is also found in the hydrolysis at 100°C using H₂O (Figure S3). The high reactivity of the deuterated hydroxy group is reasonable because of the less electron negativity of deuterium than that of hydrogen, which increases the nucleophilicity of the oxygen atom in the hydroxy group.

Other alcoholyses were also examined to further elucidate the TBD-catalyzed depolymerization of PTMC. The formation of PD was confirmed in ¹H NMR spectra (Figure S10). Ethanolysis of PTMC finished slightly faster than methanolysis (run 2 vs. run 4 in Table 2), and the reaction with 2-propanol took 1 week (168 h; run 5 in Table 2). Although the degradation does not complete, it

is interesting that *tert*-butanol serves as a nucleophile to cleave the carbonate bonds of PTMC with the aid of TBD (run 6 in Table 2). The slow reaction rates for alcoholysis with 2-propanol and *tert*-butanol are explained by steric effects. The electrostatic charges of the hydroxy oxygen atom of alcohols were estimated from density functional theory calculation, suggesting that they are scarcely involved with the reactivity of the hydroxy group. The affinity with PTMC may contribute to the difference in the reactivity between methanol and ethanol. By the same token, that between methanol and water may be partially explained by the affinity.

3.4 | Homogeneous methanolysis

2-Methyltetrahydrofuran (2-MTHF) is recognized as a green alternative to THF.³⁵ Although the solubility of PTMC is not high, depolymerization using 2-MTHF can be an option for the chemical recycling of PTMC and polycarbonates, as demonstrated in the previous study.²³ To further elucidate the mechanism of the methanolysis of PTMC using the NMR technique, homogeneous reactions in THF-*d*₈ were conducted. We studied the effect of loading ratios of the nucleophile CD₃OD to the substrate PTMC on depolymerization. TBD was used as a catalyst because it led to the complete degradation of PTMC in the inhomogeneous methanolysis. The loading of TBD was decreased to 0.01 M while PTMC loading was maintained at 10 mg to sufficiently slow the reaction for monitoring using ¹H NMR. Three major species are observed in the ¹H NMR spectra of the reaction solution in the middle of the homogeneous methanolysis (Figure S11): PD, 3-hydroxypropyl carbonates (HPC), and trimethylene biscalbonates (TMBC). The HPC structure includes hydroxy ends of PTMC and its oligomers as degradates, including BHPC. The TMBC structure corresponds to the middle parts of PTMC and its oligomers. These

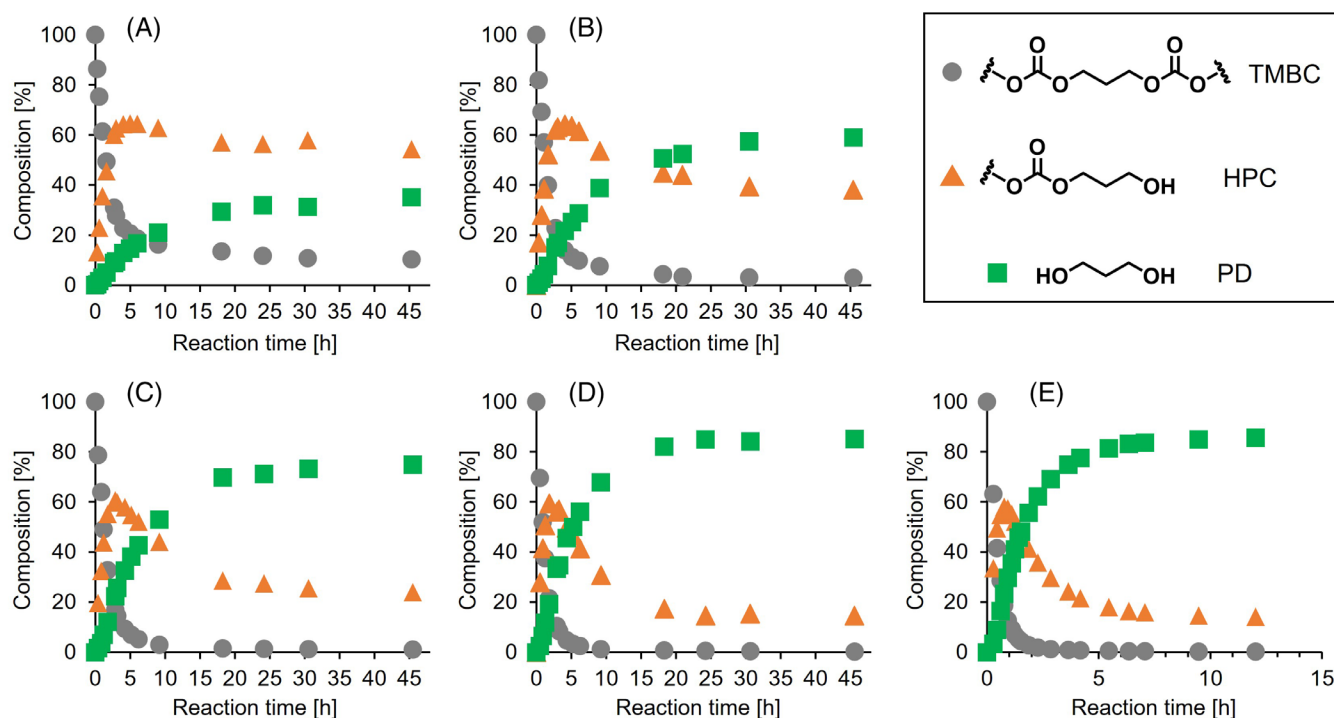


FIGURE 7 Time course of the composition of each structure in the reaction mixture of TBD-catalyzed methanolysis in THF- d_8 using different equivalents of CD_3OD relative to the repeating unit of PTMC. (A) 2, (B) 4, (C) 8, and (D, E) 16 equivalents. [TBD] = 0.01 M for all reactions. [PTMC] = 0.1 M (A–D) and 1.0 M (E).

show characteristic signals at 1.97, 1.78, and 1.64 ppm (Figure S11, insert), and thus each composition in the reaction solution was calculated from the integral ratios of these signals. The time courses of these structures were monitored by 1H NMR and are plotted in Figure 7. At the initial stage of methanolysis, the composition of TMBC sharply decreases, while the compositions of HPC and PD increase with time, suggesting the random scission of carbonate bonds by methanolysis. The ratio of HPC to PD is initially high and gradually decreases to less than 1, indicating the predominant oligomer formation at the initial stage and further decomposition of HPC to yield PD. These reaction profiles are thus consistent with those described in Figure 5, as in the case of $R = CH_3$. These reaction processes are also indicated by the time course of the 1H NMR spectra (Figure S12). The homogeneous methanolysis proceeds faster than the inhomogeneous methanolysis, as the production of HPC and PD plateaus in 24 h (Figure 7A–D) during homogeneous methanolysis, whereas the inhomogeneous methanolysis requires over 36 h to reach completion (run 1 in Table 1). Considering a TBD concentration 10 times lower than that in the inhomogeneous reactions, the reactivity of methanol to PTMC entirely dissolved in THF- d_8 becomes considerably high. The reaction plateaus faster (~ 10 h) when the PTMC concentration

increases by 10 times; the catalyst concentration is maintained at 0.01 M (Figure 7E).

The ratio of nucleophiles to the substrate affects the extent of degradation of PTMC and the production of HPC and PD. As with the alcoholysis of PET,^{22,24} the increased loading of CD_3OD results in higher production of PD. The composition of PD remains below 40% at the peak of the reaction when using 2 equivalents of CD_3OD relative to the monomer unit of PTMC (Figure 7A). The composition exceeds 80% when using 16 equivalents of CD_3OD (Figure 7D, E). The smallest unit of the HPC structure is BHPC, as confirmed by 1H and ^{13}C NMR (Figures S13 and S14). Finally, BHPC remains at a composition of approximately 15% in the reaction solution when using 16 equivalents of CD_3OD (Figure 7E). These results indicate that the methanolysis of HPC structures (oligomers and BHPC) and the reverse reaction between DMC and PD reach equilibrium (Figure 5). The reactions that used more CD_3OD correspond to runs 9 and 1 in Table 1. These reactions yield less BHPC ($\sim 9\%$ and 0%). As the CD_3OD -PTMC ratio becomes low, the probability involving PD as the nucleophile increases, which may yield trimethylene carbonate (TMC), a cyclic carbonate monomer of PTMC. The characteristic signals of TMC (Figure S15) were confirmed in 1H NMR spectra of the reaction mixture, in particular using 2 equivalents of CD_3OD relative to the monomer unit of PTMC

(Figure S16). However, the composition of TMC in the product formed is 0.3%. Thus, the formation of TMC is negligible in the TBD-catalyzed methanolysis, yielding mostly PD by high catalytic efficiency. Overall, TBD-catalyzed methanolysis of PTMC is an efficient and low-energy recycling approach. Although we also examined polymer-bound TBD as a recyclable catalyst for the hydrolysis and methanolysis of PTMC, it did not exhibit sufficient catalytic activity.

4 | CONCLUSION




We have investigated the efficacy of several organocatalysts for the depolymerization of PTMC as a base material for future sustainable materials. A phosphazene base P_2 -*t*-Bu showed relatively high catalytic activity resulting in a 22% degradation of PTMC during the course of 20 d under inhomogeneous hydrolysis. Additionally, 31% of PTMC was hydrolytically fragmented within a few hours in THF. Other catalysts, including TBD, moderately catalyzed the inhomogeneous hydrolysis of PTMC with a degradation of less than 10%. In addition to P_2 -*t*-Bu, TBD promoted the fragmentation of PTMC during the homogeneous hydrolysis in THF. The refluxed condition significantly promoted the inhomogeneous hydrolysis, achieving 20%, 89%, and 91% of the degradation of PTMC by TBD, P_2 -*t*-Bu, and DBU in 12 h, respectively. The strong basicity and anionic mechanism of P_2 -*t*-Bu may be preferable for hydrolysis. By contrast, only TBD exhibited exceptionally high catalytic activity for methanolysis of PTMC compared to the other catalysts. The catalytic potency of TBD is due to its dual hydrogen bonding mechanism. Two pragmatic routes for chemical recycling of PTMC and its analogs were suggested in this study: homogeneous hydrolysis in THF (or 2-MTHF) catalyzed by P_2 -*t*-Bu, and TBD-catalyzed methanolysis. These methods will serve as green, efficient, low-energy options for the chemical recycling of functionalized aliphatic polycarbonates with the proper selection of catalysts and solvents. Based on the present study, further developments of catalysts are desired, including those to complete hydrolysis and those recyclable and robust.

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