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Polymerization and depolymerization of polyesters and polycarbonates using 1,1,3,3-tetramethyl guanidine as a catalyst for improved resource utilization

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Despite being biodegradable materials whose random disposal has no significant impact on the environment, finding new routes to recycle polyesters and polycarbonates under the current conditions of limited resources is of high importance. This study used 1,1,3,3-tetramethylguanidine (TMG) as a catalyst to test the polymerization of polylactide and poly(hexane-1,6-diol carbonate). In addition, the depolymerization of polylactide, poly-ε-caprolactone, polyvalerolactone, polyethylene terephthalate, and poly(bisphenol A carbonate) using TMG as a catalyst was investigated. In LA polymerization, various alcohols can be employed to initiate the reaction using TMG as a catalyst. When BnOH and poly(ethylene glycol) monomethyl ether-1900 were used as initiators, highly controlled LA polymerizations were observed. In addition, TMG could depolymerize PLA, PCL, PVL, PET, and PBAC in alcohol and water to produce alcoholysis products. Compared to depolymerization using 1,8-diazabicyclo[5.4.0]undec-7-ene and 1,5,7-triazabicyclo[4.4.0]dec-5-ene as catalysts, TMG exhibited an absolute advantage over PCL, PET, and PBAC depolymerization.

Sustainability spotlight

Global annual plastic production surged from 2 million tons in 1950 to 234 million tons in 2000, reaching 460 million tons in 2019. Should alternative strategies remain unimplemented, plastic consumption is expected to reach 1.231 billion tons by 2060. Furthermore, multiple nondegradable petrochemical plastics persist in the environment for centuries due to their durability. Compared with these nondegradable petrochemical plastics, polyesters are biodegradable and environmentally friendly. Although these polyesters and polycarbonates can be decomposed by bacteria under environmental conditions, the resulting products of polymer decomposition such as water and carbon dioxide are of no economic benefit. If these plastics are to be manufactured again, they must be extracted and manufactured from plants or petroleum. Therefore, if used polymers can be transformed into small organic molecules that may be employed as starting materials for these polymers or in other applications, then such a chemical reaction holds economic significance. This study used 1,1,3,3-tetramethylguanidine (TMG) as a catalyst to test the polymerization of polylactide and poly(hexane-1,6-diol carbonate). In addition, the depolymerization of polylactide, poly-ε-caprolactone, polyvalerolactone, polyethylene terephthalate, and poly(bisphenol A carbonate) using TMG as a catalyst was investigated. In LA polymerization, various alcohols can be employed to initiate the reaction using TMG as a catalyst. When BnOH and poly(ethylene glycol) monomethyl ether-1900 were used as initiators, highly controlled LA polymerizations were observed. In addition, TMG could depolymerize PLA, PCL, PVL, PET, and PBAC in alcohol and water to produce alcoholysis products. Compared to depolymerization using 1,8-diazabicyclo[5.4.0]undec-7-ene and 1,5,7-triazabicyclo[4.4.0]dec-5-ene as catalysts, TMG exhibited a significant advantage over PCL, PET, and PBAC depolymerization.

Introduction

Plastics are artificial polymers produced by polymerizing diverse organic repeating units called monomers. Given their long-chain structure and high molecular mass, plastics possess outstanding mechanical and chemical strength and durability. Owing to their ease of development and low-cost production, plastics are widely utilized daily in various industrial and consumer applications, thus fostering positive changes in diverse life domains.

Global annual plastic production surged from 2 million tons in 1950 to 234 million tons in 2000, reaching 460 million tons in

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2019. Should alternative strategies remain unimplemented, plastic consumption is expected to reach 1.231 billion tons by 2060.[1,2] Furthermore, multiple nondegradable petrochemical plastics, including polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), and polystyrene (PS), persist in the environment for centuries due to their durability. Compared with these nondegradable petrochemical plastics, polyesters, including polylactide (PLA) and poly-ε-caprolactone (PCL), are biodegradable and environmentally friendly. Although these polyesters and polycarbonates can be decomposed by bacteria under environmental conditions, the resulting products of polymer decomposition such as water and carbon dioxide are of no economic benefit. If these plastics are to be manufactured again, they must be extracted and manufactured from plants or petroleum. Therefore, if used polymers can be transformed into small organic molecules that may be employed as starting materials for these polymers or in other applications, then such a chemical reaction holds economic significance. There is currently plenty of literature reports on the use of various catalysts for the decomposition of polyesters and polycarbonates. For example, PLA[3–13] (Fig. 1A), PCL[14–16] (Fig. 1B), polyethylene terephthalate (PET)[10e,11,4,17–19,17–20,21–25] (Fig. 1C), and polycarbonates (PCs)[13,15,26–28] (Fig. 1D) can be decomposed into small organic molecules through alcoholysis. In general, metal catalysts act as Lewis acids to activate the carbonyl group of polymers, allowing external alcohols to attack the carbonyl group of the polymers (Fig. 1E), leading to the degradation of the polymer and the formation of new ester groups. This reaction is also known as alcoholysis. Analysis revealed that the metal catalyst is stable in alcoholic solvents and under high-temperature conditions. In contrast to metal catalysts, organic catalysts exhibit relatively higher stability and eliminate the concerns of residual toxic metals.

1,1,3,3-Tetramethylguanidine (TMG) is an effective catalyst for urea formation from amine and cyanate,[29] carbon dioxide capture,[30] ring-opening polymerization of sarcosine-derived *N*-thiocarboxyanhydride,[31] carbonatation of amine and carbon dioxide,[32] *t*-butyldimethylsilylation of alcohols,[33] amide synthesis from pantolactone and amino acid,[34] Baylis–Hellman reaction,[35] epoxidation,[36] aldol reaction,[37] and advanced synthetic methodologies.[38] According to the literature, TMG demonstrated efficiency for carbonyl group activation. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)[39] and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)[40,41] which are similar to TMG, have been reported to catalyze cyclic ester polymerization. In addition, TMG is stable in the atmosphere, and it may be suitable to catalyze the alcoholysis of the polyesters. Herein, TMG was used to investigate the activity of LA polymerization and poly(hexane-1,6-diol carbonate) synthesis. In addition, TMG was used for the alcoholysis of PLA, PCL, polyvalerolactone (PVL), PET, and poly(bisphenol A carbonate) (PBAC).

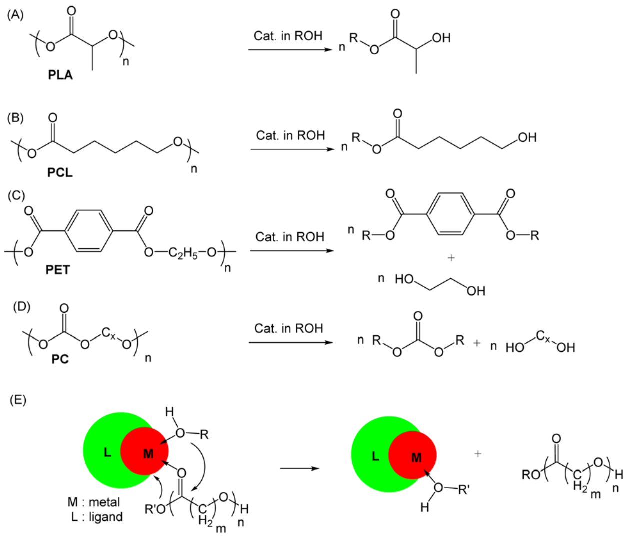

Fig. 1 Depolymerization of (A) PLA, (B) PCL, (C) PET, (D) PC, and (E) the mechanism of alcoholysis using a metal catalyst.

Results and discussion

LA polymerization with TMG as a catalyst and various initiators is outlined in Table 1. The optimal conditions for different initiators are detailed in entries 1–3 and 8–13. Notably, the LA polymerization employing benzyl alcohol (BnOH, see entry 1 of Table 1) as an initiator demonstrated a higher polymerization rate, achieving 95% conversion at 25 °C within 70 min. However, lactide polymerization occurred under the conditions specified in Table 1, entry 1, but without the addition of TMG. After one day, no formation of PLA was observed. The molecular mass characteristics for the polymerization (entry 1 of Table 1) resulted in Mn_{GPC}-5800 with a dispersity ($Đ$) value of 1.10. Similarly, the LA polymerization with tetrabutylammonium benzyl alkoxide ($N^{n}Bu_4OBn$, entry 2 of Table 1) as an initiator yielded a 95% conversion at 25 °C after 90 minutes, with Mn_{GPC}-5000 and $Đ = 1.15$. This polymerization result suggests that BnOH's proton enhances the catalytic activity of TMG for LA polymerization.

Further analysis of the role of H–OBn was conducted using LA polymerization with mono-deuterated benzyl alcohol (BnOD, entry 3 of Table 1), and the lower catalytic activity with BnOD was observed compared to BnOH (entry 1 of Table 1), as indicated by the kinetic isotope effect (KIE) calculated to be $k_{BnOH}/k_{BnOD} = 22.21$. This result indicates that the bond dissociation of H–OBn occurs at the transition state during the LA polymerization process.

Additionally, the LA polymerization using TMG without BnOH (entry 6 of Table 1) revealed a lower polymerization rate compared to the LA polymerization with BnOH (entry 1 of Table 1). This discrepancy suggests that the polymerization mechanisms differ significantly with and without BnOH, as the rate of LA polymerization using TMG alone is substantially lower. When the LA concentration was increased to 0.5 M (entry 4 of Table 1), the catalytic activity increased by approximately four-fold, achieving a conversion of 93% after 24 minutes. When the LA polymerization was performed in $CDCl_3$ without drying by molecular sieve in the atmosphere (entry 7 of Table 1), the polymerization time increased from 70 to 85 min compared to that in dry $CDCl_3$ (entry 1 of Table 1). The results implied that

Table 1 L-Lactide polymerization using TMG as a catalyst[a]

Entry	TMG + initiator initiator=	Time (min)	Conv. (%)[b]	Mn_{Cal}[c]	Mn_{NMR}[b]	Mn_{GPC}[d]	$Đ$[d]	k_{obs}[b] × 10^4 (error) min^{-1}
1	BnOH	70	95	6900	6600	5800	1.10	421 (5)
2	$N^{n}Bu_4OBn$	98	95	6900	6700	5000	1.15	286 (8)
3	BnOD	1200	91	6600	6300	5000	1.12	20 (1)
4[e]	BnOH	24	93	6800	6200	6000	1.12	898 (11)
5[e]	$N^{n}Bu_4OBn$	34	93	6800	6500	5800	1.18	542 (7)
6[f]	TMG only	300	94	6900	6600	4700	1.18	49 (2)
7[g]	BnOH	85	93	6800	6300	5600	1.12	306 (63)
8	IPA	480	92	6700	6400	5500	1.19	55 (5)
9	^{t}BuOH	600	90	6600	4500	4400	1.41	41 (1)
10	PEG_{4000}	360	89	6500	7100	5000	1.14	59 (1)
11	MeOPhOH	210	93	6800	6500	4100	1.29	129 (2)
12	ClPhOH	900	94	6900	7500	5500	1.32	31 (6)
13	HFIPA	1560	92	6700	6100	4100	1.18	18 (4)
14[h]	BnOH	360	96	7000	6500	5100	1.14	101 (4)
15[i]	BnOH	2160	95	6900	6500	4400	1.12	15 (1)
16[j]	BnOH	480	92	6700	6400	5600	1.13	55 (1)
17[k]	BnOH	10	93	13 500	11 000	8500	1.14	—[m]
18[l]	PEG_{4000}	180	95	10 800	9100	9300	1.10	—[m]
19[k]	DBU + BnOH	5	97	14 100	12 400	9400	1.21	—[m]
20[k]	TBD + BnOH	7	95	13 400	12 400	9400	1.23	—[m]
21[k]	DMAP + BnOH	180	94	13 600	11 600	8900	1.13	—[m]

[a] Reaction conditions: [LA]:[TMG]:[I] = 50 : 1 : 1, 2 mL of $CDCl_3$, [LA] = 0.25 M, at 25 °C. [b] The kinetic data were studied through ^{1}H NMR analysis. Mn_{NMR} is calculated from the molecular weight of LA times the ratio (the integration of the peak at 5.2 ppm × 5/the integration of the peak at 7.3 ppm × 2) and adds Mw(BnOH). [c] Calculated from the molecular weight of LA times the ratio of ($[LA]_0/[BnOH]_0$), the conversion percentage, and finally adds Mw(BnOH). [d] Obtained through gel permeation chromatography (GPC) analysis and calibration using the polystyrene standard. Values of Mn_{GPC} are the values obtained from GPC times 0.58. [e] [LA] = 0.5 M in $CDCl_3$, at 25 °C. [f] [LA] = 1 M in $CDCl_3$ without BnOH, at 25 °C. [g] The reaction was performed in the atmosphere. [h] In toluene (2 mL). [i] In tetrahydrofuran (2 mL). [j] In 1,2-dichlorobenzene (2 mL). [k] Neat reaction. LA = 1.44 g (10 mmol), BnOH = 0.011 g (0.1 mmol), Cat. = 0.1 mmol at 110 °C. [l] Neat reaction. LA = 1.44 g (10 mmol), PEG_{4000} = 0.8 g (0.2 mmol), Cat. = 0.1 mmol at 110 °C. [m] Not determined.

the presence of moisture slightly reduced the LA polymerization rate with TMG. In addition, various alcohols, including isopropanol (IPA), *tert*-butyl alcohol, polyethylene glycol 4000 (PEG 4000), 4-methoxyphenol (MeOPhOH), 4-chlorophenol (ClPhOH), and hexafluoro-2-propanol (HFIPA), were used as initiators to investigate their polymerization rate (entries 8–13 of Table 1). The ^{1}H NMR spectra of PLA oligomers synthesized at a ratio of 5 : 1 : 1 (LA : TMG : initiator) are shown in Fig. S9–S14, and the chain-end signals observed in the ^{1}H NMR spectra demonstrated that these alcohols can act as initiators. The results revealed that the electron-withdrawing group in alcohols decreased the catalytic activity (MeOPhOH > ClPhOH; IPA > HFIPA), and the steric bulk around the alcohols group also decreased the catalytic activity (IPA > ^{t}BuOH). The optimization of the reaction solvents, including toluene, tetrahydrofuran (THF), and 1,2-dichlorobenzene, is also studied as summarized in entries 1 and 16–18 of Table 1. The results revealed that TMG exhibited the highest catalytic activity in deuterated chloroform, whereas it dipped to its lowest in THF. This is presumably due to the hydrogen bond between TMG and THF. In adherence to green chemistry principles towards solvent-free reactions, the neat reactions were carried out with BnOH (entry 17 of Table 1) and PEG_{4000} (entry 18 of Table 1) as initiators. A tremendous catalytic activity of TMG under neat conditions with highly controllable polymerization were observed. Compared with the catalytic activity of LA ROP for other commercially available organocatalysts, including DBU, TBD, and 4-(*N*,*N*-dimethylamino)pyridine (DMAP), comparative results are presented in entries 19–21 of Table 1. There is not much difference between the catalytic activities of DBU, TBD, and TMG. DBU has the best catalytic activity (5 min, conversion = 97%) compared with TBD (7 min, conversion = 95%) and TMG (10 min, conversion = 93%). DMAP exhibited the lowest catalytic activity of LA ROP (180 min, 94%).

The results of entries 1 to 7 in Table 2 revealed the highly controlled LA polymerization with narrow dispersity ($Đ$) values ranging from 1.06 to 1.24, highlighting excellent living properties by using TMG as a catalyst. However, the experimental molecular masses (Mn_{GPC}) are always lower than the theoretical masses (Mn_{Cal}). This phenomenon may be attributed to TMG also acting as an initiator, as supported by the data shown in Table 1, entry 6. To test this hypothesis, TMG was reacted with 5 equivalents of LA in $CDCl_3$, and the resulting mixture was analyzed using MALDI-TOF mass spectrometry (Fig. S17). The results confirmed that TMG can indeed serve as an initiator to attack LA. The lower Mn_{GPC} values compared to the Mn_{Cal} values are likely due to an excess amount of initiators (BnOH + TMG). Considering that TMG alone without BnOH exhibits much lower activity (Table 1, entry 6), increasing the amount of BnOH might suppress the initiation role of TMG, thereby bringing the Mn_{GPC} values closer to the Mn_{Cal} values. Experimental results (Table 2, entries 8–12) supported this hypothesis:

Table 2 Living property of L-LA polymerization using TMG as a catalyst and BnOH as an initiator[a]

Entry	[LA] : [TMG] : [BnOH]	Time (min)	Conv. (%)[b]	Mn_{Cal}[c]	Mn_{NMR}[b]	Mn_{GPC}[d]	Đ[d]
1	50 : 1 : 1	70	95	6900	6800	5400	1.11
2	100 : 1 : 1 (entry 1 + 50 LA)	92	98	14 200	9000	7300	1.06
3	150 : 1 : 1 (entry 2 + 50 LA)	102	96	20 800	14 200	12 500	1.16
4	200 : 1 : 1 (entry 3 + 50 LA)	116	97	28 000	19 500	17 200	1.15
5	250 : 1 : 1 (entry 4 + 50 LA)	240	98	35 400	23 800	20 700	1.18
6	300 : 1 : 1 (entry 5 + 50 LA)	420	96	41 600	26 500	25 300	1.2
7	350 : 1 : 1 (entry 6 + 50 LA)	630	95	47 800	31 300	30 200	1.24
8	50 : 1 : 2	60	96	3600	3500	3300	1.24
9	50 : 1 : 3	45	95	2400	2300	2200	1.15
10	100 : 1 : 2	105	96	7000	6900	7400	1.06
11	200 : 1 : 2	240	93	13 500	12 400	12 100	1.43
12	300 : 1 : 2	480	90	19 500	18 400	18 600	1.16

[a] Reaction conditions: [TMG] = 1.15 mM in $CDCl_3$ (2 mL), 72 mg LA for every loading, at 25 °C. [b] Data were obtained through ^1H NMR analysis. Mn_{NMR} is calculated from the molecular weight of LA times the ratio (the integration of the peak at 5.2 ppm × 5/the integration of the peak at 7.3 ppm × 2) and adds Mw(BnOH). [c] Calculated from the molecular weight of LA times the ratio of ($[LA]_0/[BnOH]_0$), the conversion percentage, and finally adds Mw(BnOH). [d] Obtained through gel permeation chromatography (GPC) analysis and calibration using the polystyrene standard. Values of Mn_{GPC} are the values obtained from GPC times 0.58.

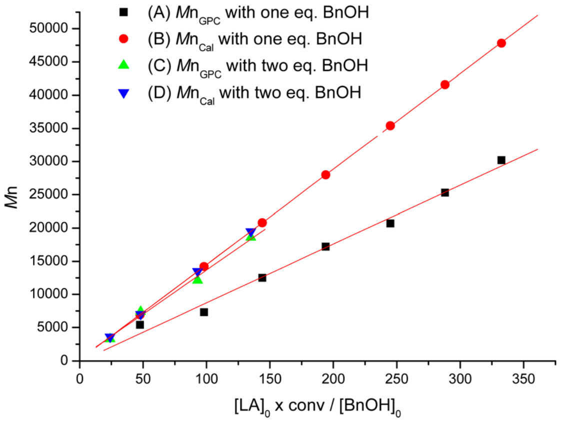

Fig. 2 Linear plots of (A) Mn_{GPC} *versus* ($[LA]_0$ × conv./$[BnOH]_0$) using one eqn BnOH, represented by black squares; (B) Mn_{Cal} *versus* ($[LA]_0$ × conv./$[BnOH]_0$) using one eqn BnOH, represented by red dots; (C) Mn_{GPC} *versus* ($[LA]_0$ × conv./$[BnOH]_0$) using two eqn BnOH, represented by green triangles; and (D) Mn_{Cal} *versus* ($[LA]_0$ × conv./$[BnOH]_0$) using two eqn BnOH, represented by blue inverted triangles.

when the amount of BnOH was increased to two equivalents, the initiation role of TMG was successfully suppressed, and the Mn_{GPC} values of the resulting PLA reached much closer to the Mn_{GPC} values, as shown by the linear relationship between Mn_{GPC} and $[LA]_0$ × conv./[BnOH], assuming BnOH functions as initiators in the polymerization process (Fig. 2C).

To support the practicality of using TMG as a catalyst for LA polymerization, TMG was used with poly(ethylene glycol) monomethyl ether-1900 ($mPEG_{1900}$) to synthesize "polyethylene glycol monomethyl ether-1900-*b*-poly-L-lactide" ($mPEG_{1900}$-*b*-PLA), which is a material commonly used for drug delivery[43] as

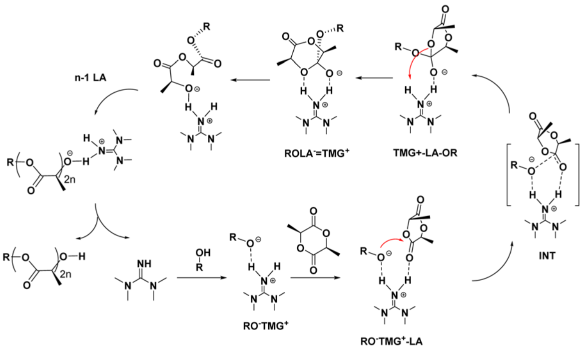

Fig. 3 Possible mechanism of LA polymerization using TMG as a catalyst.

Table 3 Synthesis of $mPEG_{1900}$-*b*-PLA using TMG as a catalyst and $mPEG_{1900}$ as an initiator[a]

Entry	$mPEG_{1900}$: LA	Conv. %	Time (min)	Mn_{cal}[b]	Mn_{NMR}[c]	Mn_{GPC}[d]	Đ
1	1 : 30	97	35	6100	7000	5900	1.03
2	1 : 60	90	130	9800	9800	9400	1.04
3	1 : 70	96	180	11 600	11 300	11 200	1.09
4	1 : 80	93	220	12 600	12 800	12 600	1.08
5	1 : 100	80	400	13 400	13 800	13 100	1.04
6[e]	1 : 60	96	80	10 200	9800	11 600	1.19
7[f]	1 : 60	0	130	—[g]	—[g]	—[g]	—[g]

[a] Reaction conditions: DCM, [TMG] = 0.025 M at 25 °C. [b] Calculated from the molecular weight of LA times the ratio of ($[LA]_0/[BnOH]_0$), the conversion percentage, and finally adds Mw($mPEG_{1900}$). [c] Data were obtained through ^1H NMR analysis. Mn_{NMR} was calculated from the molecular weight of LA times the ratio (the integration of the peak at 5.2 ppm/the integration of the peak at 3.38 ppm) and adds Mw($mPEG_{1900}$). [d] Obtained through GPC analysis and calibration based on the polystyrene standard. Values of Mn_{GPC} are the values obtained from GPC molecular weight. [e] Using DBU as an initiator. [f] Using TBD as an initiator. [g] Not available.

shown in Table 3. The linear relationship between Mn_{GPC} and ($[LA]_0 \times$ conv.)/[BnOH] (entries 1–5 of Table 3) presented in Fig. 3 illustrates the excellent living property of LA polymerization using TMG [$Đ$ values (1.03–1.09)], despite using a large molecular mass $m\mathrm{PEG}_{1900}$ as an initiator. Under the reaction conditions described in entry 2 of Table 3, catalytic data for DBU and TBD (entries 6 and 7 in Table 3) indicate that DBU displays superior catalytic activity (80 min, 96% conversion) compared to TMG; in contrast, TBD is inactive in the LA polymerization when $m\mathrm{PEG}_{1900}$ is used as the initiator.

Kinetic study of LA polymerization

Experiments with the $[LA]_0$/[TMG]/[BnOH] ratios of 50 : 1 : 1, 50 : 1 : 2, 50 : 1 : 3, 50 : 1 : 4, 50 : 1 : 6, 50 : 2 : 1, 50 : 3 : 1, 50 : 4 : 1 and 50 : 6 : 1 ([LA] = 0.25 M in 2 mL $CDCl_3$ at 25 °C) were performed. As detailed in Tables S1–S2, the kinetic results revealed a first-order dependency on the [LA] concentration, revealing that one LA was initiated in every polymerization cycle according to eqn (1), where k_{obs} is equal to $k_{prop}[TMG]^x[BnOH]^y$, and k_{prop} is the propagation rate constant. To determine the order of [TMG] (x), the polymerization conditions of different [TMG] (5, 10, 15, 20, and 30 mM) with the same [LA] (0.25 M) and [BnOH] (5 mM) were conducted (Fig. S4). Since [BnOH] is considered as a constant, it is incorporated into k_1 ($k_1 = k_{prop}[BnOH]^y$) as described by eqn (2). After ln k_{obs} values were plotted against ln [TMG] (eqn (3), Fig. S6), the k_1 value was calculated to be 1.15 $M^{-0.63}min^{-1}$, and the order of [TMG] (x) is 0.63. Furthermore, various concentrations of [BnOH] (5, 10, 15, 20, and 30 mM) with the same [LA] (0.25 M) and [TMG] (5 mM) (Fig. S5) were screened. When [TMG] is regarded as a constant, it is incorporated into k_2 ($k_2 = k_{prop}[TMG]^x$) (eqn (4)). After ln k_{obs} values were plotted against ln [BnOH] (eqn (5), Fig. S6), k_2 was calculated to be 0.40 $M^{-0.44}min^{-1}$, and the order of [BnOH] (y) is 0.44. Next, k_{prop} was calculated to be 11.56 $M^{-1.07}min^{-1}$ by averaging $k_1/[BnOH]^{0.44}$ and $k_2/[TMG]^{0.63}$. LA polymerization using [TMG] and [BnOH] followed an overall kinetic law given by eqn (6).

$$-d[LA]/dt = k_{obs}[LA] = k_{prop}\,[LA][TMG]^x[BnOH]^y \quad (1)$$

$$k_{obs} = k_{prop}\,[TMG]^x[BnOH]^y = k_1[TMG]^x \quad (2)$$

If [BnOH] is a constant

$$\ln k_{obs} = \ln k_1 + x \ln[TMG] \quad (3)$$

$$k_{obs} = k_{prop}\,[TMG]^x[BnOH]^y = k_2[BnOH]^y \quad (4)$$

If [TMG] is a constant

$$\ln k_{obs} = \ln k_2 + y \ln[BnOH] \quad (5)$$

$$-d[LA]/dt = 9.91\,[LA][TMG]^{0.42}[BnOH]^{0.61} \quad (6)$$

In summary of the experimental activation parameters, the LA polymerizations using TMG as a catalyst and BnOH as an initiator were investigated at 25 °C, 35 °C, 45 °C, 55 °C, and 65 °C as shown in Table S6. The Eyring plot of $\ln[k\,T^{-1}]$ *versus* $1\,T^{-1}$ shown in Fig. S8 revealed an activation enthalpy ($\triangle H^{\ddagger}$) of 19.40 kJ mol^{-1} and entropy ($\triangle S^{\ddagger}$) of −0.21 kJ mol^{-1} K^{-1}. The estimated Gibbs free energy of activation of 82.0 kJ mol^{-1} at 298 K is relatively low.

Proposed mechanism of LA polymerization

According to the literature, DBU[39] first forms a hydrogen bond with the alcohol, and the hydrogen on this hydrogen bond then forms another hydrogen bond with the carbonyl group of the monomer. Subsequently, the oxygen atom of the alcohol attacks the carbonyl group of the monomer, leading to the formation of a four-membered acetal ring. TBD[40] forms a hydrogen bond between the hydrogen atom on its nitrogen and the carbonyl group of the monomer, while another nitrogen atom forms a hydrogen bond with the alcohol. Subsequently, the oxygen atom of the alcohol attacks the carbonyl group of the monomer, resulting in the formation of a six-membered acetal ring. Herein, the study of the interaction between TMG and BnOH was investigated and is shown in Fig. S18. The proton of the methylene group of BnOH shifted to 4.65 ppm (singlet) from 4.68 ppm (doublet, $J = 4.0$ Hz), and the proton on the nitrogen atom of TMG disappeared. This indicates the formation of a hydrogen bond between BnOH and TMG. Inspired by the literature, the possible mechanism of LA polymerization using TMG as a catalyst is illustrated in Fig. 3. In the beginning, TMG interacts with BnOH through the N⋯H–O hydrogen bond to be RO^-TMG^+. Then, LA enters to form the reactant complex (RO^-TMG^+–LA) through another N–H⋯O bond. During the following nucleophilic addition of BnOH to LA, TMG deprotonates BnOH to increase the BnO^- nucleophilicity, forming a charge-separated intermediate INT. This unstable charge-separated state "INT" rapidly transforms into a more stable complex (TMG^+–LA–OR). Then, the LA ring's ether oxygen interacts with N–H bond's terminal proton to form a new six-membered ring $ROLA^- = TMG^+$. Because of the activation of the ether oxygen of the LA ring through the interaction of the O^{ether}–H–N bond, the LA ring opens to afford a new alcohol that will interact with TMG for the next LA ring opening. According to the high KIE value ($k_{BnOH}/k_{BnOD} = 22.21$ from entry 1 *vs.* entry 3 in Table 1) for the LA polymerization, the H–OBn bond dissociation/association is likely involved in intermediate INT.

Poly(hexane-1,6-diol carbonate) synthesis from hexane-1,6-diol and dimethyl carbonate polymerization

Poly(hexane-1,6-diol carbonate) is an aliphatic polycarbonate synthesized from 1,6-hexanediol and carbonates such as dimethyl carbonate (DMC) or diphenyl carbonate (DPC) *via* polycondensation. It functions as the soft segment in thermoplastic poly(carbonate-urethane) elastomers, imparting elasticity and improving durability. This diol contributes to enhanced stability against hydrolysis and oxidation, making it suitable for use in flexible and long-lasting materials like adhesives, coatings, and elastomers. Poly(hexane-1,6-diol carbonate)[42] is a valuable component in the synthesis of high-performance polyurethane materials, offering a balance of flexibility and durability.

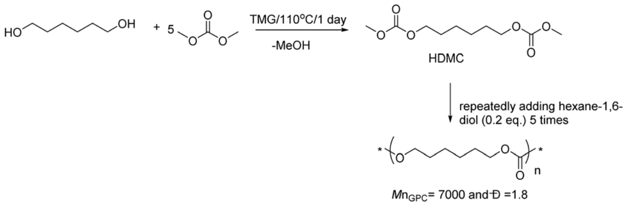

Fig. 4 Synthesis of poly(hexane-1,6-diol carbonate).

Based on TMG's strong ability to activate the carbonyl group for esterification, the synthesis of poly(hexane-1,6-diol carbonate) using TMG as a catalyst was investigated. Initially, hexane-1,6-diol and dimethyl carbonate (1 : 1 ratio) are mixed, and then TMG is added as a catalyst at 110 °C in a round-bottom flask equipped with a Dean–Stark apparatus to remove the resulting methanol. However, only hexane-1,6-diyl dimethyl bis(carbonate) (HDMC) was produced after the reaction was refluxed after a day, and no polymer was produced. To improve the polymerization yield, the new polymerization method (Fig. 4) was investigated. The mixture of HDMC (10.00 g, 42.73 mmol), hexane-1,6-diol (2.00 g, 16.69 mmol), and TMG (0.05 g, 0.43 mmol) was set at 110 °C, and the produced methanol was removed by a Dean–Stark apparatus after 2 h. Consumption of hexane-1,6-diol was monitored by ^{1}H NMR and 2.00 g of hexane-1,6-diol was employed. After repeatedly adding hexane-1,6-diol for the fifth time, the liquid in the round-bottom solidified and the magnet could no longer stir. The produced poly(hexane-1,6-diol carbonate) was purified through extraction [H_2O/dichloromethane (100 mL/100 mL) × 3] as a white wax-like solid (yield = 90% with Mn_{GPC} = 7000 and $Đ$ = 1.8) and confirmed by ^{1}H and ^{13}C NMR (Fig. S17). When a mixture of hexane-1,6-diol and dimethyl carbonate was heated at 110 °C without TMG for one day, hexane-1,6-diyl dimethyl bis(carbonate) was not formed. Furthermore, combining hexane-1,6-diyl dimethyl bis(carbonate) with hexane-1,6-diol in the absence of TMG and heating at 110 °C for one day did not result in any polymerization. Compared to reaction conditions employing metal salt catalysts reported in the literature,[42b,43] this method using TMG as a catalyst not only operates at a lower polymerization temperature but also requires a shorter polymerization time.

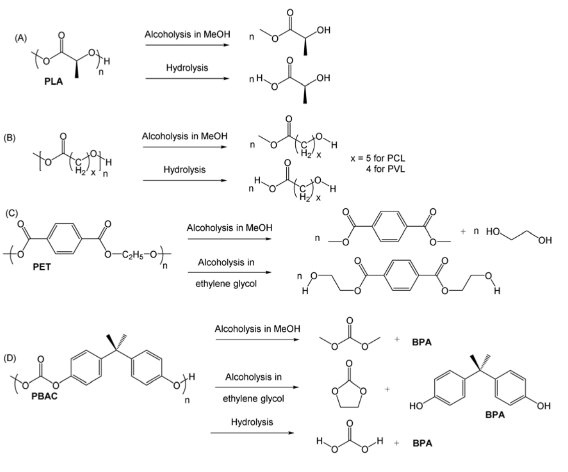

Fig. 5 Alcoholysis and hydrolysis of PLA, PCL, PVL, PET, and PBAC.

Depolymerization of polylactide, poly-ε-caprolactone, polyethylene terephthalate, and poly(bisphenol A carbonate) using TMG as a catalyst

TMG was systematically evaluated for its efficacy in the alcoholysis of PLA, PCL, PVL, PET, and PBAC in a sealed tube, and the alcoholysis of these polymers is illustrated in Fig. 5. The product of the alcoholysis of PLA in methanol is methyl lactate, and the product of the hydrolysis of PLA is lactic acid (Fig. 5A). The products of the alcoholysis of PCL and PVL in methanol are methyl 6-hydroxyhexanoate and methyl 5-hydroxypentanoate, respectively, and the products of the hydrolysis of PCL and PVL are 6-hydroxyhexanoic acid and 5-hydroxypentanoic acid (Fig. 5B). The alcoholysis of PET using methanol and ethylene glycol yields dimethyl terephthalate and bis(2-hydroxyethyl) terephthalate, respectively (Fig. 5C). Since the hydrolysis of PET produces terephthalic acid, which is insoluble in organic solvents and thus difficult to purify, it was not studied further. The products of the alcoholysis of PBAC in methanol are dimethyl carbonate and bisphenol A (BPA). The alcoholysis of PBAC using ethylene glycol yields ethylene carbonate and BPA. The products of the hydrolysis of PBAC are carbonic acid and

Table 4 Depolymerization of PLA, PCL, PVL, PET, and PBAC using TMG as a catalyst[a]

Entry	Polymer	Reaction condition	Time[g] (min)
1[b]	PLA (Mn = 11 000 kg mol^{-1})	Alcoholysis with MeOH	80
2[b]		Hydrolysis	420
3[c]	PCL (Mn = 4000 kg mol^{-1})	Alcoholysis with MeOH	540 (91%)
4[d]	PVL (Mn = 24 900 kg mol^{-1})	Alcoholysis with MeOH	600
5[e]	PET (Mn = 24 000 kg mol^{-1})	Alcoholysis with MeOH	180
6[e]		Alcoholysis with ethylene glycol	270
7[f]	PBAC (Mn = 17 500 kg mol^{-1})	Alcoholysis with MeOH	30
8[f]		Alcoholysis with ethylene glycol	60
9[f]		Hydrolysis	180

[a] Reactions were performed in a closed 20 mL sealed tube with TMG (0.1 mmol) at 60 °C. Depolymerization conversion was identified through ^{1}H NMR analysis. Time refers to the complete depolymerization and makes the polymer unobservable. 2 mL of solvents were used for the alcoholysis of methanol, ethanol, water, and ethylene glycol. [b] 0.72 g of PLA was used. [c] 0.57 g of PCL was used. [d] 0.5 g of PVL was used. [e] 0.90 g of PET was used. [f] 1.3 g of PBAC was used. [g] Depolymerization time with 100% conversion.

Table 5 Depolymerization of PLA, PCL, PVL, PET, and PBAC using various organocatalysts[a]

		Depolymerization time with 100% conversion		
Entry	Polymer	DBU	TBD	TMG
1	PLA	3 min	18 h	80 min
2	PCL	—[b]	—[b]	9 h (91%)
3	PVL	30 min	12 h	10 h
4	PET	—[b]	—[b]	3 h
5	PBAC	185 min	—[b]	30 min

[a] Reaction conditions: The polymers (5 mmol), solvent (50 mmol), and catalyst (0.1 mmol) were taken in a sealed tube and heated at 60 °C. [b] Depolymerization was not obtained after 2 d.

BPA. The results revealed that TMG can depolymerize five polymers in methanol. The degradation rates of these five polymers are as follows: PBAC > PLA > PET > PCL > PVL.

The comparative results of depolymerization using various organocatalysts were investigated as summarized in Table 5. The results revealed that three commercially available organocatalysts have their depolymerization advantages for different polymers. The results of PLA depolymerization (entry 1 of Table 4) show that DBU has an absolute advantage with only 3 minutes to complete PLA depolymerization compared to TBD (18 h) and TMG (80 min). Similar results also occurred in PVL depolymerization (entry 2 of Table 4, 30 min for DBU, 12 h for TBD, and 10 h for TMG). However, TMG exhibited its absolute advantage over PCL, PET, and PBAC depolymerization in that PCL and PET can only be degraded by TMG. Furthermore, the short depolymerization time of PBAC only needed 30 min using TMG as a catalyst compared to that of DBU (165 min) and TBD (inactive). The depolymerization results revealed that $O^{-}TMG^{+}$ (Fig. 3) was effective in activating the carbonyl group of various polymers.

Conclusions

Commercially available TMG exhibited great catalytic activity for highly controlled LA ROP in toluene at 25 °C and 110 °C under neat conditions. In addition, various alcohols, such as PEG, could be used as initiators for LA ROP. Poly(hexane-1,6-diol carbonate) also could be produced from hexane-1,6-diyl dimethyl bis(carbonate) and hexane-1,6-diol by using TMG as a catalyst. Moreover, TMG could depolymerize PLA, PCL, PVL, PET, and PBAC in alcohol and water to generate alcoholysis and hydrolysis products. Compared to DBU and TBD, TMG exhibited an absolute advantage over PCL, PET and PBAC depolymerization. Faced with society's current need for many polyesters and polycarbonates, TMG may satisfy roles as a catalyst to promote polymerization and as an agent to effectively degrade these polymers.

Author contributions

R. K., T.-Y. L., F. H., and M. R. T. performed the experiments; T. B. H. performed additional edits and proofreading; H.-C. T and S. D. performed NMR measurements; and H.-Y. C. conceptualized the project, wrote and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information: Kinetic and experimental data supporting this article have been included as part of the SI. See DOI: https://doi.org/10.1039/d5su00245a.

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