Synthesis of Polycarbonates and Polyesters via Tetraalkylammonium Salt-catalyzed Ring-opening Polymerization

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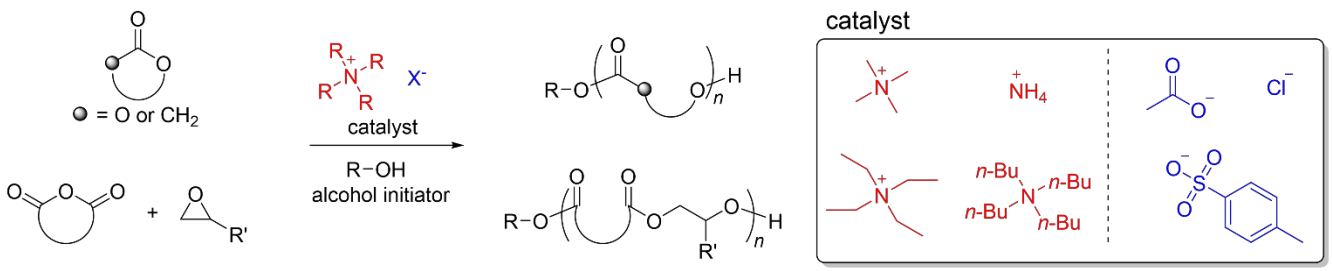
Abstract

Tetraalkylammonium salt was found to be an effective catalyst for the ring-opening polymerization of cyclic carbonates and cyclic esters, yielding aliphatic polycarbonates and polyesters with narrow dispersities. An important feature of this catalytic system is its tunable catalytic ability, which was achieved by altering the alkyl substrates and counter anions. The catalytic mechanism was studied by ^{1}H NMR spectroscopy.

Keywords: Ring-opening (co)polymerization, Aliphatic polycarbonate/polyester, Tetraalkylammonium salt

Graphical abstract



Aliphatic polycarbonates and polyesters are well-known for their high (bio)degradability, unlike the aromatic and semi-aromatic ones.[1–5] Therefore, they attract intensive research attention for various applications, such as environmentally benign packaging materials and biocompatible and bioresorbable materials for medical implants.[6–10] To synthesize aliphatic polycarbonates and polyesters, ring-opening polymerization (ROP) of the corresponding cyclic monomers is one of the most important methods. Tin(II) 2-ethylhexanoate [$Sn(Oct)_2$] is the most widely used catalyst for ROP in the industry. Tin-free polymers (< 1 ppm tin) are also required for biomedical applications, such as drug delivery carriers, and have been approved by the FDA. Driven by both scientific interest and market demand, the development of safe catalysts, mainly organocatalysts such as heterocyclic carbenes,[11–14] organic acids,[14–16] organic bases,[17,18] and natural compounds,[19,20] has been the focus of research in recent years for the preparation of metal-free polycarbonates and polyesters.[21,22]

In addition to these organocatalysts, we identified a new group of catalysts, namely, alkali metal carboxylates (AMCs),[23–25] which were found to be simple, easy to handle, and industrially relevant catalysts for ROP and ring-opening copolymerization (ROCOP). The successful development of AMCs has allowed us to explore other catalyst structures by altering the anion and cation components. Organic ammonium salts were the first candidates that were considered. Trimethyl glycine, a natural betaine first found in sugar beets, shows catalytic activity in the ROP of trimethylene carbonate (TMC).[26] Other than trimethyl glycine, tetramethyl ammonium acetate also shows excellent catalytic activity.

It is worth mentioning that some previous studies have used tetraalkylammonium salts as initiators or catalysts in the ROP of cyclic esters. Tetraalkylammonium salts have been utilized as initiators in the ROP of β-butyrolactone by Jedliński *et al.*[27] Guo *et al.* tested the ROP of δ-valerolactone (VL) using tetrabutylammonium chloride and tetrabutylammonium fluoride as the catalysts, although in solution polymerization, the reactivity at room temperature was low.[28] Recently, Pang *et al.* reported that for the ROP of L-lactide (LLA) and ε-caprolactone (CL) in bulk polymerization at high temperatures, tetrabutylammonium fluoride shows

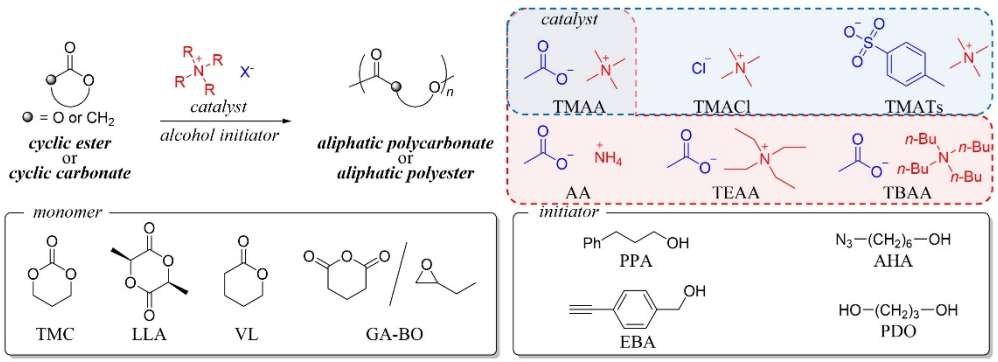


Fig. 1. Tetraalkylammonium salt-catalyzed ROP of cyclic carbonate and cyclic ester to synthesize aliphatic polyesters.

Table 1. ROP of TMC catalyzed by TMAA and other catalysts [a]

run	cat.	$[M]_0/[I]_0$ /[cat.]	time (min.)	conv. (%) [b]	$M_{n,theo.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ$ [d]	TOF (h^{-1})
1	TMAA	50/1/0.1	5	74.0	3,900	4,300	6,140	1.13	4,400
2	AA	50/1/0.1	120	4.0	— [e]	— [e]	— [e]	— [e]	10
3	TEAA	50/1/0.1	10	83.7	4,410	4,060	6,440	1.21	2,500
4	TBAA	50/1/0.1	10	83.9	4,420	3,960	7,240	1.22	2,500
5	TMACl	50/1/0.1	30	87.8	4,600	4,640	7,800	1.21	880
6	TMATs	50/1/0.1	180	28.5	1,600	1,430	2,440	1.36	48
7	TMAA	50/1/0.01	60	65.6	3,490	3,580	5,240	1.17	3,300
8	TMAA	50/1/0.001	600	70.0	3,710	3,930	5,930	1.18	3,500
9	TMAA	50/0/0.1	55	39.6	— [e]	— [e]	29,000	1.42	220

[a] Polymerization conditions: atmosphere, Ar; temperature, 70 °C; initiator, PPA; monomer, TMC. [b] Determined by ^{1}H NMR spectroscopy of the obtained polymer in $CDCl_3$. [c] Calculated from $[TMC]_0/[PPA]_0$ × conv. × (M.W. of TMC) + (M.W. of PPA). [d] Determined by SEC of the crude product in THF using PSt standards. [e] Not determined.

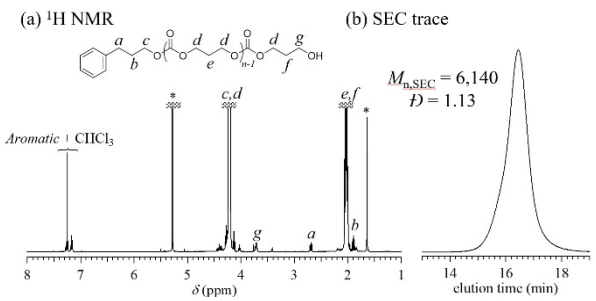


Fig. 2. (a) ^{1}H NMR spectrum (recorded in $CDCl_3$; the asterisk indicates solvent) and (b) SEC trace (eluent, THF; flow rate, 1.0 mL min^{-1}) of PTMC (run 1 in Table 1).

superior catalytic reactivity than other halides.[29] However, in most previous studies, the investigation of catalyst candidates has been limited to tetrabutylammonium salts. Moreover, neither has the correlation between catalyst structure and activity been studied nor the monomer scope assessed.

By harnessing the promising catalytic ability of tetramethylammonium salts,[26] we systematically investigated the effects of both ammonium and the counterion in the ammonium salt catalyst on ROP and ROCOP to synthesize aliphatic polycarbonates and polyesters (**Figure 1**). The reaction mechanisms were also investigated. In this study, we conducted a detailed investigation into the catalytic ability and activity of quaternary ammonium salts, aiming to developing a highly active catalyst system with a broad monomer applicability.

Our investigation began with catalyst screening using various tetraalkylammonium salts in the ROP of TMC (**Table 1**). Commercially available tetramethylammonium acetate (TMAA) was used as the catalyst. The polymerization was conducted with 3-phenyl-1-propanol (PPA) as an initiator at an initial $[TMC]_0/[PPA]_0/[TMAA]$ ratio of 50/1/0.1 at 70 °C in the bulk (run 1 in **Table 1**). After 5 min, the monomer conversion ($conv._{TMC}$) reached 74.0%. By analyzing the ^{1}H NMR spectrum of the isolated poly(trimethylene carbonate) (PTMC), the molecular weight ($M_{n,NMR}$) was calculated to be 4,300, which closely matches the theoretical molecular weight ($M_{n,theo.}$ = 3,900) calculated based on the monomer conversion (**Figure 2a**). Using size exclusion chromatography (SEC) analysis, the SEC molecular weight ($M_{n,SEC}$) and dispersity index ($Đ$) were determined to be 6,140 and 1.13, respectively (**Figure 2b**). Based on these results, the TMAA-catalyzed ROP of TMC proceeded successfully without any evident side reactions.

After this initial success, the catalytic activities of three other ammonium acetate salts with different alkyl substitutions (*i.e.,* ammonium acetate (AA), tetraethylammonium acetate (TEAA), and

Table 2. TMAA-catalyzed ROP of various cyclic esters [a]

run	M [b]	$[M]_0/[PPA]_0/[TMAA]$	time (h)	conv. (%) [c]	$M_{n,theo.}$ [d]	$M_{n,NMR}$ [c]	$M_{n,SEC}$ [e]	$Đ$ [e]
1	LLA	50/1/0.1	55	82.8	6,100	5,330	6,010	1.16
2	LLA	25/1/0.1	15	82.1	3,100	3,540	4,750	1.13
3	LLA	100/1/0.1	170	71.1	10,400	9,280	10,100	1.19
4	CL	50/1/0.1	90	6.3	—	—	—	—
5	VL	50/1/0.1	140	63.4	3,310	3,120	5,100	1.10

[a] Polymerization conditions: atmosphere, temp., 100 °C; Ar; initiator, PPA; catalyst, TMAA; $[M]_0/[PPA]_0/[TMAA]$ = 50/1/0.1. [b] M: monomer. [c] Determined by ^{1}H NMR spectroscopy of the obtained polymer in $CDCl_3$. [d] Calculated from $[M]_0/[PPA]_0 \times$ conv. × (M.W. of M) + (M.W. of PPA). [e] Determined by SEC of the crude product in THF using PSt standards.

tetrabutylammonium acetate (TBAA)) were evaluated (runs 2–4 in **Table 1** and **Scheme S1**). When AA was used as the catalyst, the polymerization rate was significantly lower, with only 4.0% of TMC converted after 120 min (run 2 in **Table 1**). This result suggests that alkyl substitution of ammonium was essential for polymerization. TEAA and TBAA catalyze the ROP of TMC with a similar efficacy as that of TMAA, with a turnover frequency (TOF) of 2,500. SEC measurement of the obtained PTMC showed a relatively narrow $Đ$ of 1.21–1.22 (runs 3 and 4 in **Table 1**). These results demonstrate that the alkyl substitutions (methyl, ethyl, and butyl) of ammonium do not significantly affect the catalytic ability and controllability of polymerization.

Next, the effect of the counter anion on the ammonium salt was examined (runs 5 and 6; **Table 1** and **Scheme S2**). Tetramethylammonium chloride (TMAC) and tosylate (TMATs) were used under the same polymerization conditions. As a result, the TOF value decreased in the order of $AcO^- > Cl^- > TsO^-$. This indicates that the catalytic activity and basicity of the catalysts have a strong relationship: the higher the basicity of the counter anion, *viz.,* the higher the pK_a value of the conjugated acid, the higher the catalytic activity (**Figure S1**).[30–32] As the counter anions are most likely to interact with the hydroxy group at the propagating chain end,[29] the basicity of the counter anion could influence the catalytic efficiency to a large extent (**Scheme S3**).

After the catalyst screening, TMAA was selected as the optimal catalyst for further study because of its high activity, simple structure, commercial availability, and absence of β-hydrogen for possible Hofmann elimination side reactions. When the amount of the catalyst was reduced to a $[PPA]_0/[TMAA]$ ratio of 1/0.01 and 1/0.001, the ROP of TMC proceeded equally well with narrow dispersity, although an extended polymerization time was required (runs 7 and 8 in **Table 1**). The PTMC obtained in run 8 was analyzed using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (**Figure S2**). In addition to the major series of peaks assignable to PTMC initiated by PPA with a hydroxy chain end, another minor series of peaks was observed corresponding to the PTMC initiated by 1,3-propanediol (PDO), which was generated by the hydrolysis of TMC, followed by the release of CO_2 (**Scheme S4**). This indicates that the ROP of TMC can proceed successfully with an extremely small amount of catalyst (26 ppm TMC weight). When the ROP of TMC was conducted without the addition of an alcohol initiator, $conv._{TMC}$ reached 39.6% after 55 min (run 9 in **Table 1**). The obtained product was confirmed to be the PTMC initiated by PDO via MALDI-TOF MS analysis. Importantly, the one originating from the acetate anion was not detected (**Figure S3**). This further demonstrated that the ROP of TMC was initiated by an alcohol initiator instead of TMAA.

To examine the scope of the monomer, ROPs of three representative cyclic esters (LLA, CL, and VL) were investigated. The ROP of LLA was conducted at an $[LLA]_0/[PPA]_0/[TMAA]$ ratio of 50/1/0.1 at 100 °C (run 1 in **Table 2**). After 55 h, $conv._{LLA}$ reached 82.8%. ^{1}H NMR and SEC analysis suggested that the obtained PLLA includes a PPA initiating end-group with a narrow dispersity ($Đ$ = 1.16; **Figure S4**). MALDI-TOF MS analysis of the obtained PLLA also revealed only one series derived from PLLA with a PPA end group, indicating that the TMAA-catalyzed ROP of LLA successfully suppressed transesterification (**Figure S5**). In addition, the molecular weight of PLLA was controlled by altering the initial $[LLA]_0/[PPA]_0$ ratio to 25 and 100 while maintaining the dispersity at a similar level (runs 2 and 3 in **Table 2**; **Figure S6**). The analysis shown in **Figure S7a** demonstrates a linear relationship between monomer conversion and $M_{n,SEC}$. All of these experimental data support the living polymerization nature and the suppression of side reactions. Additionally, the logarithmic kinetic plot ($\ln([M]_0/[M]_t$–Time) indicates that the ROP proceeded in the first-order kinetic of monomer concentration (**Figure S7b**).

When the ROP of CL was attempted at 100 °C, the consumption of CL reached only 6.3% after 90 h (run 4 in **Table 2**). When the monomer was changed to VL, 63.4% was converted after 140 h. Despite the low reaction rate, the polymerization was well controlled,

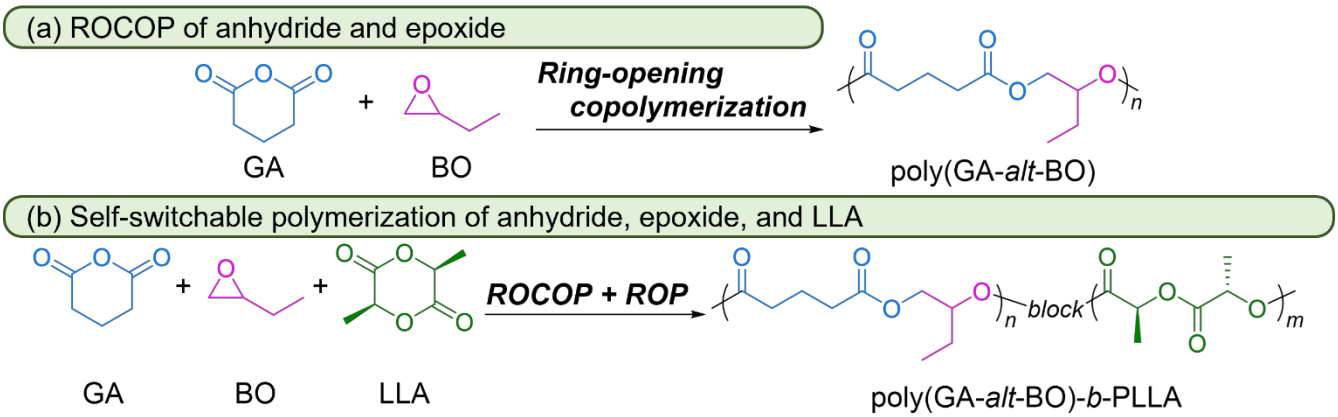


Fig. 3. Ring-opening copolymerization (ROCOP) and self-switchable polymerization of monomer mixtures.

with a dispersity index of 1.10 (run 5 in **Table 2**; **Figure S8**).

Other than the ROP of cyclic esters, the ring-opening copolymerization (ROCOP) of cyclic anhydrides and epoxides represents an important alternative approach for the controlled synthesis of various aliphatic and semi-aromatic polyesters (**Figure 3a**).[33–39]

The catalytic ability of TMAA for ROCOP was examined using glutaric anhydride (GA) and butylene oxide (BO) with an initial $[GA]_0/[BO]_0/[PPA]_0/[TMAA]$ ratio of 50/150/1/0.1 (run 1 in **Table S1**). After the polymerization at 100 °C for 14 h, 79.3% of GA was converted, and the obtained polymer has an $M_{n,SEC}$ of 3,700 with $Đ$ = 1.29. This indicates that TMAA can also be applied to the ROCOP of cyclic anhydrides and epoxides (**Figure S9**).

After the successful ROP of cyclic esters and ROCOP of cyclic anhydrides and epoxides, these two polymerizations were integrated using a monomer mixture of GA, BO, and LLA to achieve self-switchable polymerization (**Figure 3b**; run 2 in **Table S1**).[40] After allowing the reaction to proceed for 17 h at 100 °C, $conv._{GA}$ and $conv._{LLA}$ were detected to be 81.4% and < 3%, respectively. After an additional 7.5 h, the complete conversion of GA and a 59.8% conversion of LLA were achieved. This indicates that the ROP of LLA began after GA had been almost fully consumed (**Figure S10**), resulting in the corresponding block copolymer, poly(GA-*alt*-BO)-*b*-PLLA, which might contain a minimally tapered region. Thus, TMAA was successfully applied not only to ROP and ROCOP but also to self-switchable polymerization (**Figure S11**).

The functional group tolerances of the initiators were also evaluated. When alcohol initiators with azido and alkynyl moieties were employed, the ROP of LLA catalyzed by TMAA proceeded smoothly, similar to the reaction using PPA as the initiator (runs 1 and 2 in **Table S2** vs. run 1 in **Table 2** and **Figures S12** and **S13**). These reactive functional groups can be further utilized for chain-end modification after polymerization. In addition to the mono-alcohols, PDO, a diol, also initiated the ROP of

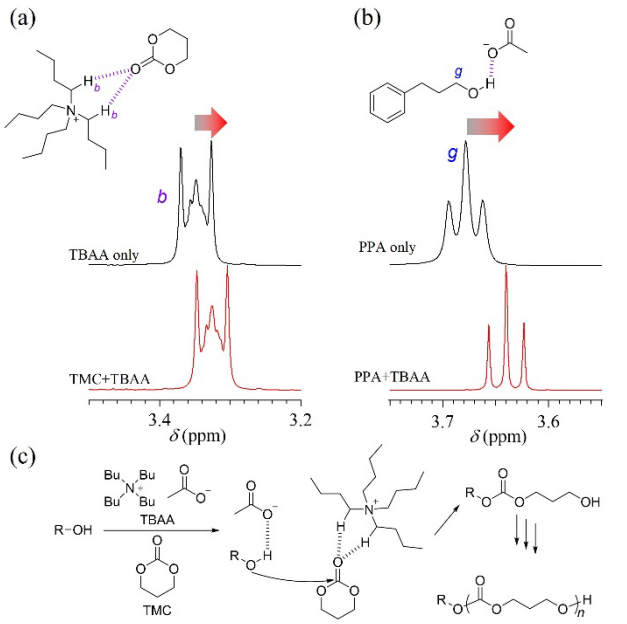


Fig. 4. ^{1}H NMR spectra of (a) TBAA in the absence (black line; 100 mmol L^{-1}) and presence of TMC (red line; [TBAA] = 100 mmol L^{-1}; [TBAA]/[TMC] = 1/1) and (b) PPA in the absence (black line; 100 mmol L^{-1}) and presence of TBAA (red line; [TBAA] = 100 mmol L^{-1}; [TBAA]/[TMC] = 1/1) in $CDCl_3$. (c) Dual activation mechanism of TBAA-catalyzed ROP.

LLA in an equally well-controlled manner (run 3 in **Table S2** and **Figure S14**). To gain insights into the reaction mechanism, the interactions between the catalyst, monomer, and initiator (propagating chain end) were qualitatively evaluated by ^{1}H NMR measurements on a 1:1 mixture of TBAA with PPA and TMC. TBAA was selected for the mechanistic study because of its higher solubility in $CDCl_3$ than in TMAA. By comparing the ^{1}H NMR spectrum of the 1:1 mixture of TBAA and TMC with the spectrum of TBAA alone, a slight upfield shift of the protons at the *α*-position of tetrabutylammonium (*b*) was observed, which indicates that the electron density increased upon mixing with TMC (**Figures 4a**, **S15**, and **S16**). Similar behaviors have been reported when tetraalkylammonium salt was mixed with halogen atom[41] and imine[42]. These results support the fact that the *α*

protons of TBAA activate the TMC monomers. Previous studies have also suggested that the α protons act as a Brønsted acid. A comparison of the ^{1}H NMR spectrum of the 1:1 mixture of TBAA and PPA with that of PPA alone shows a significant upfield shift of the methylene protons adjacent to the hydroxyl group (Figures 4b, S16, and S17). This indicates a strong hydrogen bonding interaction between the acetate anion and the hydroxyl group. Additionally, Figure S18a presents the NMR spectra obtained by varying the mixing ratio of TBAA and TMC. The results demonstrate that the increase in the shift of TBAA is dependent on the amount of catalyst added. This suggests that the interaction between the ammonium salt and TMC is in equilibrium rather than a very tight complexation. In the case of the spectra of the catalyst and alcohol, the tendency is abnormal probably due to the interference of other hydrogen bond donors like water, which is difficult to remove completely (Figure S18b). Additionally, we previously reported alcohol activation by carboxylate anions via Fourier transform infrared (FT-IR) spectroscopy.[23] These results confirmed the dual activation of both the monomer and initiator (propagating chain end) by tetraalkylammonium acetate catalysts. Figure 4c shows the expected catalytic mechanism based on dual activation.

In conclusion, tetraalkylammonium acetates have been demonstrated to be effective catalysts for the ROP of cyclic carbonates and cyclic esters. They can also be utilized in the ROCOP of cyclic anhydrides and epoxides and even in self-switchable polymerization, which combines different catalytic polymerization cycles. Therefore, these simple catalysts can be used in the syntheses of polycarbonate and polyester materials without metal residue contamination.

Supplementary data

Supplementary material is available at *Chemistry Letters*

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Conflict of interest statement. None declared.

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