Macromolecules

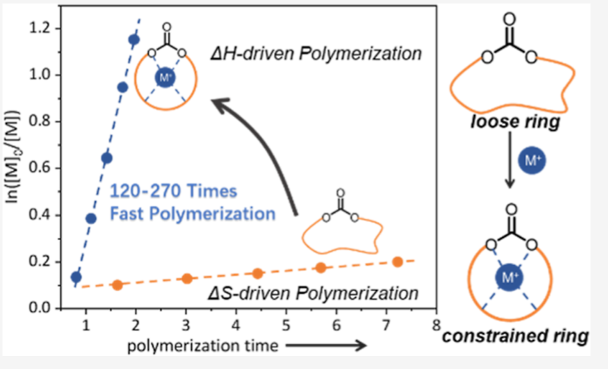
pubs.acs.org/Macromolecules Article

Understanding Alkali Cation-Assisted Ring-Opening Polymerization of Macrocyclic Carbonate: Kinetics and Thermodynamics

Yuanyuan Qu, Junyuan Hu, Fengzhen Guo, Dong Ji, Yuguang Li, Zhenjiang Li, Yunsheng Xu, Jin Huang,* Lili Zhao,* and Kai Guo*

Cite This: Macromolecules 2023, 56, 6790−6797 Read Online

ABSTRACT: Control over polymerization thermodynamics and kinetics enables the generation of polymers with on-demand properties. This is exemplified by the ring-opening polymerization of tetraethylene glycol carbonate (4EGMC) using an alkali cation (M^+)-based binary catalytic system at ambient temperature. By introducing a guanidine catalyst [(1,5,7-triazabicyclo[4.4.0]dec-5-ene), TBD], the alkali cation-assisted ring-opening polymerization of macrocyclic carbonate was *ca.* 120−270 times faster than the reaction without an alkali cation, M^+ (0.16−0.36 min^{-1} with M^+ vs 0.001 min^{-1} without M^+). Moreover, the interaction between 4EGMC and M^+ led to an increase in the ring strain, supported by both bench experiments and computational simulations. This interaction altered the driving force of polymerization from the change of entropy to enthalpy, which revealed the pivotal role of alkali cations in regulating the ring-opening polymerization of macrocyclic carbonate.



INTRODUCTION

Engineering polymers with on-demand physical properties through controllable polymerization accelerates the innovation in polymer production.[1−3] Ring-opening polymerization (ROP),[4−6] one of the most important methods of polymerization, has been applied to the generation of versatile polymers.[7−13] For cyclic monomers including lactides, lactones, etc., polymerization occurs through an ester bond[14] assisted by both the release of the ring strain and the change of conformational and translational entropy, yielding a well-defined polymer structure. While the field in the design of benign catalytic systems to active ester bonds, thereby kinetically regulating the polymerization, is significantly developed,[15−20] studies focusing on modulating the thermodynamics to influence the outcome of polymerization remain a challenge, resulting from the ring strain and the change of enthalpy, ΔH_p, of a given cyclic structure are difficult to be affected by external conditions.

Among the available experimental conditions to control equilibrium chain growth polymerization thermodynamics, changing solvents and/or initial monomer concentrations to enhance the solvation effect[21−23] between the monomer, polymer, and solvent were recently reported.[24] Albertsson et al. demonstrated the thermodynamics correlated with the surrounding solvent medium, where polymerization in toluene had a high ΔH_p value in comparison to that in acetonitrile (−22.0 vs −10.1 kJ·mol^{-1}, 1 M initial concentration of monomer). The hypothetical explanation of this result was that the interaction between solvents and monomers affected the monomer conformations, thereby driving the change of ring strain, thus leading to the change in thermodynamics.[25] Lately, an in-depth understanding reported by Odelius et al. revealed that both monomer−solvent and polymer−solvent interactions contributed to thermodynamics.[26] Apart from the solvation effect, we may ask what other conditions could be controlled to manipulate the ring strain and ΔH_p?

Some of us have recently developed a simple approach to access macrocyclic carbonates (MCs) through the selective depolymerization of polycarbonates. The ring structures of attained MCs were associated with little to no ring strains, thus leading to entropy-driven ROP of MCs.[27,28] We hypothesize that the thermodynamics of ROP might be altered to be enthalpy-driven through constraining MCs by the supramolecular interaction with auxiliary, thus increasing the ring strain and ΔH_p. To this end, inspired by the electrostatic interaction between the crown ether and an alkali cation (M^+)[29−31] yielding a supramolecular complex to alter the ring strain of crown ether,[32,33] an ethyleneoxy-substituted macrocyclic carbonate (tetraethylene glycol carbonate, 4EGMC) to

Received: July 3, 2023
Revised: July 31, 2023
Published: August 18, 2023

https://doi.org/10.1021/acs.macromol.3c01311
Macromolecules 2023, 56, 6790−6797

Scheme 1. Solvation Effect Leads to the Difference in Polymerization Thermodynamics and Our Work Using Alkali-Based Catalysts to Control Both Thermodynamics and Kinetics

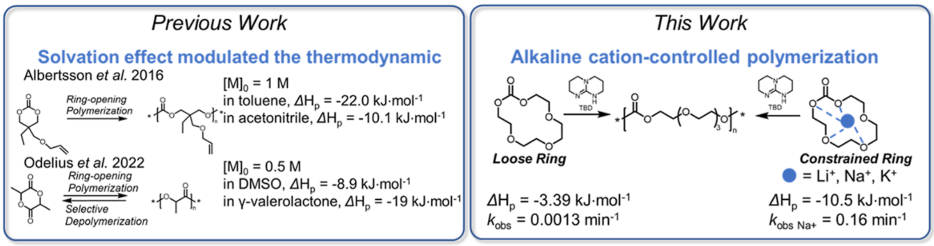


Table 1. Ring-Opening Polymerization of 4EGMC Using TBD with $NaPF_6$ at Ambient Temperature[a]

entry	$[I]_0/[TBD]_0/[Na^+]_0/[M]_0$	t/min	conv. (%)[b]	$M_{n\ theo}$ (kg mol^{-1})[c]	$M_{n\ NMR}$ (kg mol^{-1})[b]	$M_{n\ SEC\ THF}$ (kg mol^{-1})[d]	$Đ_{THF}$[d]	$M_{n\ SEC\ DMF}$ (kg mol^{-1})[e]	$Đ_{DMF}$[e]
1	1/1/2/20	30	94	4.2	4.3	5.9	1.15	10.3	1.40
2	1/1/0/20	24 h	79	3.6	3.7	5.6	1.11	10.8	1.23
3	1/0/2/20	30	0	-	-	-	-	-	-
4	1/1/0.4/20	30	45	2.1	2.1	5.3	1.10	7.2	1.24
5	1/1/1/20	30	82	3.7	3.6	5.8	1.14	12.9	1.20
6	1/1/3/20	30	94	4.2	4.0	5.9	1.15	13.4	1.19
7	1/1/5/50	60	96	10.6	12.5	6.6	1.23	16.6	1.22
8	1/1/10/100	120	94	20.8	24.0	7.1	1.27	17.6	1.22

[a]Conditions: $[M]_0$ = 1 M, rt in THF, TBD and $NaPF_6$ as the catalysts, and BnOH as the initiator. [b]Determined by ^{1}H NMR in $CDCl_3$, conv. = $I_{4.28}/(I_{4.28} + I_{4.38}) \times 100\%$, $M_{n\ NMR}$ = DP × 220 + 108. [c]Theoretical molecular weight of $M_{n\ theo}$ = conv.× $([M]_0/[I]_0) \times 220 + 108$. [d]THF SEC with polystyrene standards. [e]DMF SEC with polystyrene standards.

imitate crown ether was designed, aiming to verify our hypothesis that the thermodynamics of ROP of 4EGMC can be modulated by an auxiliary. We here combined commercially available organocatalysts (1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD) with alkali cations (lithium, Li^+, sodium, Na^+, and potassium, K^+) as a binary catalytic system for ROP of 4EGMC. To our surprise, using TBD/M^+, not only thermodynamics can be modulated but also the kinetics depicted fast polymerization, ca. 120−270 times over TBD-catalyzed ROP. The polymerization was investigated through both bench and theoretical studies, revealing the key role of the alkali cation for kinetics and thermodynamics (Scheme 1).

■ RESULTS AND DISCUSSION

In the initial investigation into the alkali cation-based binary catalytic system for ROP of 4EGMC, TBD in combination with a commercially available cheap salt was employed such as sodium hexafluorophosphates ($NaPF_6$). The anion of $[PF_6]^-$ was selected due to its nature of a noncoordinating counterion in solution affording the negligible weak interaction with a cation.[34] The initial ROP of 4EGMC was performed in tetrahydrofuran (THF) using benzyl alcohol (BnOH) as the initiator and TBD/$NaPF_6$ as the catalyst at ambient temperature with a ratio of $[\text{initiator}]_0/[\text{TBD}]_0/[NaPF_6]_0/[\text{MC}]_0$ = 1:1:2:20. After 30 min, the ^{1}H NMR analysis of an aliquot of reaction mixture revealed the generation of poly(tetraethylene glycol carbonate), P4EGMC, with a high conversion of 4EGMC (94 mol %) and a M_n value of 5.9 kg mol^{-1} with a narrow dispersity ($Đ_M$ = 1.15) characterized by SEC (Table 1, entry 1, and Figure S1). To examine the activity of binary catalysts, control experiments using either TBD or a sodium cation (Na^+), at the same conditions, were performed, respectively. While TBD showed slow kinetics (79 mol % after 24 h), no conversion of 4EGMC was observed when catalyzed by $NaPF_6$, demonstrating the synergic activity of TBD and Na^+ (Table 1, entries 2 and 3). While M_n characterized by NMR ($M_{n\ NMR}$) was consistent with theoretical M_n ($M_{n\ theo}$), M_n determined by SEC ($M_{n\ SEC\ THF}$, Figure S2) was not correlated with $M_{n\ NMR}$ and the molecular weight design (Table 1, entries 4−8), resulting from the interaction between the resulting polymer, THF eluent, and stationary phase causes anomalous elution[35−38] such that polycarbonates with both low and high molecular weight were eluted together, commonly seen in a branched polymer.[39] To compare the influence of elution on P4EGMC in different solvents, we applied dimethylformamide (DMF) as the eluent for SEC analysis. A similar elution behavior that $M_{n\ SEC\ DMF}$ showed no correlation with $M_{n\ NMR}$ was revealed. The structure of P4EGMC obtained by Na^+-assisted ROP was revealed by matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF). The main population of the polymer was associated with a constant repeating unit distribution (m/z = 220.09, 4EGMC), accompanied by a minor population derived from transesterification with tetraethylene glycol as the chain ends (Figure S3).

To understand this synergic catalyzation process, the interaction between 4EGMC and Na^+ needs to be explored. Crown ether enables to bind to a certain cation forming a stable complex through an electrostatic interaction between lone pairs of electrons of oxygen atoms on the ring and the cation.[40−42] We therefore postulated that 4EGMC with high electron density could accommodate Na^+ to yield a complex. ^{1}H NMR spectroscopy analysis of the mixture of 4EGMC/Na^+ with different ratios depicted a maximum downfield shift of α proton of the carbonate group by +0.079 ppm, demonstrating the interaction between 4EGMC and Na^+ (Figure S4). Moreover, Job's plot depicted a maximum at χ = 0.5, revealing a complex with a 1:1 ratio of 4EGMC and Na^+ in the solution (Figure 1, top). To explore the structure of complexes, the single crystal obtained by X-ray diffraction was applied as a

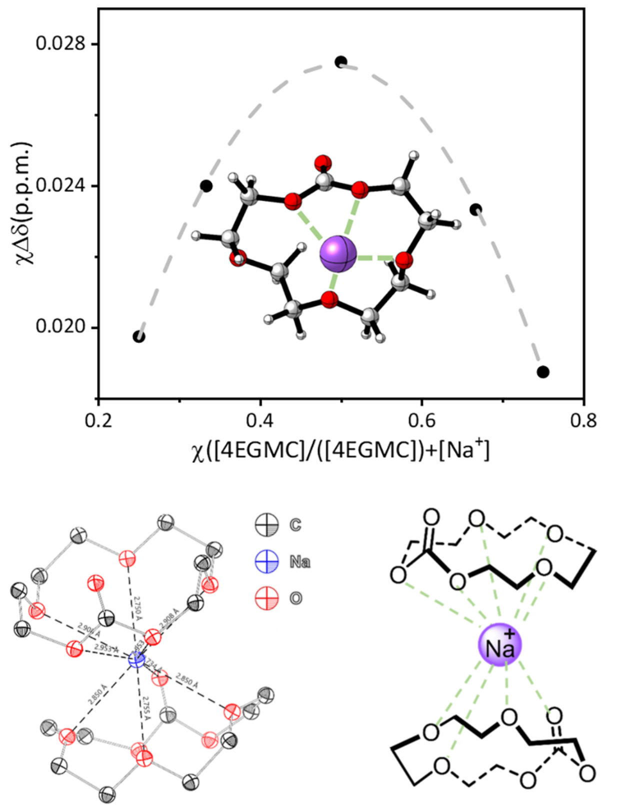


Figure 1. Job plot was obtained from ^{1}H NMR measurements of 4EGMC with $NaPF_6$, $[4EGMC]_0$ = 0.1 M in CD_3CN, top; crystal structure of 4EGMC/Na^+ with illustrated chemical structure, and protons were omitted, bottom.

reference. Complexes revealed a 1:2 ratio of Na^+ and 4EGMC, where Na^+ was located between two 4EGMC molecules (Figure S5), coordinating with both sp^2- and sp^3-hybridized oxygens of 4EGMC (Figure 1, bottom). Yet, this finding on ratios differs from the results of Job's plot, suggesting that Na^+ is located either above or below the ring with a 1:1 ratio.

As the location of Na^+ cannot be simply determined, we sought to search the possible conformation of complexes through DFT simulation using Gaussian 16 at the B3LYP-GD3/6-311+G(2d,p) level. Na^+ was initially placed above and below the ring, in which the angle between **O9**, **Na32**, and **O30** was settled and subsequently scanned to large angles step by step (Figure S6a). The increases of angle enabled the change of energies on conformation, where the highest energy was revealed in both experiments, while Na^+ presented at the interior of 4EGMC, suggesting that the cavity size of the ring was not capable to Na^+. Notably, the conformations with relative low energy were determined, while Na^+ was located both below (**C1**) and above 4EGMC (**C2**) (Figure S6b), where **C2** had lower energy by 17.6 kcal·mol^{-1} than **C1** (Figure S6c).

An alkali cation binding crown ether yields a notable increase in the dihedral angle of $-OCH_2CH_2O-$,[43] thereby yielding a constrained cyclic ether. We hypothesized that such fast ROP of 4EGMC using TBD/Na^+ could be explained by the transformation of the thermodynamic-driven force, i.e., entropy-driven to enthalpy-driven polymerization, where ROP of 4EGMC was partially assisted by the releasing of ring strain (i.e., the enthalpy change of polymerization, ΔH_p).[44,45] To determine the $\Delta H_{p\ Na^+}$ of ROP of 4EGMC catalyzed by TBD/Na^+, experiments were performed at different temperatures with a ratio of $[I]_0/[TBD]_0/[NaPF_6]_0/[M]_0$ = 1:1:2:20, $[M]_0$ = 0.5 M, in THF. The experimental results revealed a $\Delta H_{p\ Na^+}$ of −10.5 kJ·mol^{-1}, approximately 3 times higher than that of polymerization in the absence of Na^+ (ΔH_p = −3.39 kJ·mol^{-1}, Figure S7), suggesting that the coordination between Na^+ and macrocycle afforded a significant increase in the ring strain and ΔH_p. The theoretical study by the isodesmic ring-opening[46] of the macrocycle at the B3LYP-GD3/6-311+G(2d,p) (PCM, solvent = THF) level was performed. The calculated results revealed **C2** associated with a relatively low ring strain ($\Delta\Delta H_{\text{ring strain C2}}$ = −2.2 kcal·mol^{-1}), whereas Na^+ below the ring (**C1**) enabled the increase in the ring strain ($\Delta\Delta H_{\text{ring strain C1}}$ = −21.0 kcal·mol^{-1}) in comparison to no Na^+-involved polymerization ($\Delta\Delta H_{\text{ring strain}}$ = −7.8 kcal·mol^{-1}) (Table S1), consistent with the results of bench experiments ($\Delta H_{p\ Na^+}$ of −10.5 kJ·mol^{-1} vs ΔH_p = −3.39 kJ·mol^{-1}). These bench and theoretical studies therefore demonstrated that **C1** kinetically contributes to ROP of 4EGMC, albeit **C1** is associated with a relatively high conformational energy (Figure S6). Notably, the single-crystal structure of 4EGMC suggested that the ring strain was changed where the dihedral angle of the atom of $O-CH_2-CH_2-O$ was significantly influenced by the addition of Na^+ (Figure S8). Moreover, the thermal behavior of the complex (4EGMC/Na^+) characterized by differential scanning calorimetry (DSC) revealed multi-broad exothermic and endothermic peaks, while 4EGMC consisted of single melting and a broad crystallization peak (Figure S9).

In combination with the structural understanding of complexes between 4EGMC and Na^+ (**C1**), we sought more insight into the mechanism of Na^+-assisted ROP through structure−activity investigations. Buchard et al. reported ROP of six-membered carbonate that the alcoholysis carbonate through a tetrahedral intermediate mediated by the hydrogen bonds of TBD,[46,47] we assumed a similar bifunctional activation mechanistic pathway where two distinct transition states were afforded. In this catalytic pathway, the tetrahedral carbonate intermediate was formed via nucleophilic addition from an alcohol catalyzed by TBD (**TS1**) before the ring-opening of the tetrahedral intermediate (**TS2**). The reaction can proceed either by the direct interaction between alcohol, TBD, and MC or by the assistance of Na^+ with the aforementioned three species. The DFT modeling of these two pathways were therefore performed. The energy profiles of **TS1** and **TS2** demonstrated that Na^+ was a key cocatalyst to this reaction with the favored thermodynamic stability in intermediates and transition states, which were stabilized by *ca.* 12−28 kcal·mol^{-1} relative to no Na^+-involved catalytic system (Figure S10). While the rate-determining step for the TBD-catalyzed reaction was the ring-opening of the tetrahedral intermediate (**Int3**) at **TS2** for 14 kcal·mol^{-1} consistent with the previous report,[47] the nucleophilic addition to carbonate was the rate-determining step at **TS1** with 6.7 kcal·mol^{-1} for the TBD/Na^+-catalyzed reaction (Figure S10). Notably, the **TS1** of **C2**-involved catalytic pathway required a rather high energy barrier (**C2**, 11.5 kcal·mol^{-1} vs **C1**, 6.7 kcal·mol^{-1}, Figure S11) further concreting the conclusion that **C1** is the critical complex for ROP with a fast kinetic.

In the initial step, Na^+ enabled stabilization of the reaction complexes to yield **Int1**. With the reaction proceeding, the TBD/Na^+-catalyzed reaction allowed a lower energy barrier (Δ = 6.75 kcal·mol^{-1}) for **TS1**, whereas only the TBD-involved reaction required 10.38 kcal·mol^{-1} to overcome the barrier. In

https://doi.org/10.1021/acs.macromol.3c01311
Macromolecules 2023, 56, 6790−6797

the reverse reaction of TBD-catalyzed nucleophilic addition, Δ = 3.21 kcal·mol^{-1} is sufficient to form a macrocycle and TBD/initiator complex (Figure 2a), which corroborates with the experimental result that the TBD-catalyzed ROP of 4EGMC is associated with a slow kinetics, *ca.* 120 times slower than the TBD/Na$^+$-mediated reaction. As such, we assume that Na$^+$ chelates to both the macrocycle and the initiator, thereby lowering the energy barrier for **TS1**. The interaction region indicator (IRI) for **TS1** demonstrated that Na$^+$ from the macrocyclic complex interacted with the initiator through a relatively strong coordination (Figure 2b). Notably, the analysis of WBI revealed the interaction between Na$^+$, and the initiator (WBI = 0.38) was superior as compared to the coordination with the macrocycle (WBI = 0.15−0.26) (Figure 2c).

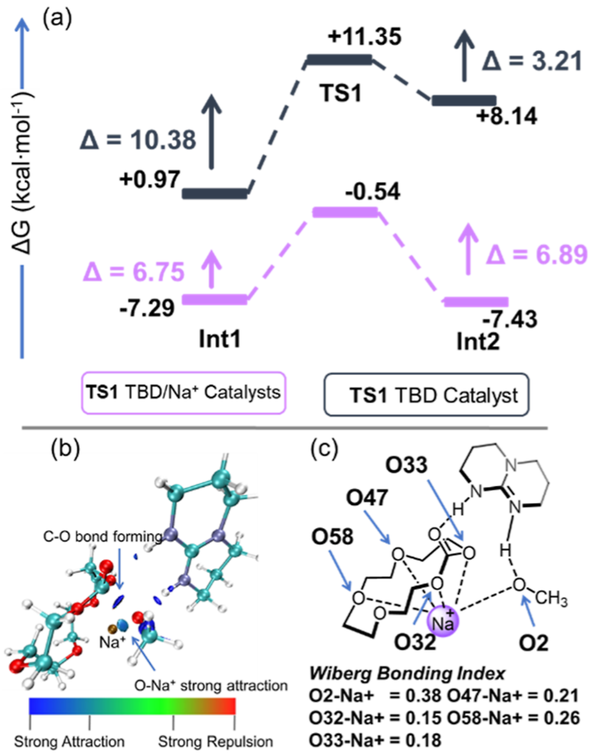


Figure 2. (a) Energetic profiles with optimized structures for both TBD- and TBD/Na$^+$-catalyzed nucleophilic addition; methanol was used as the initiator to reduce the cost of calculation; (b) selected region of the isosurface map of IRI for the transition state (**TS1**) reveals the strong interaction between Na$^+$ and methoxide;[48] and (c) analysis of WBI suggests that the interaction between methoxide and Na$^+$ is strong over the oxygen on the 4EGMC ring.

With the insight into the mechanism of alkali-assisted ROP, we postulate that 4EGMC might affiliate one of alkaline cations (Li$^+$, Na$^+$, and K$^+$) in prior.[42] Thus, the effect of different cations on the catalytic efficiency was examined (Li$^+$, Na$^+$, and K$^+$). Job's plots of Li$^+$ or K$^+$ with 4EGMC revealed a similar complex to Na$^+$/4EGMC (i.e., 1:1 ratio between the cation and the macrocycle) (Figures 3a,b, S12, and S13). Nevertheless, the strongest interaction was revealed between lithium and 4EGMC through the analysis of WBI, concluding an order of affinities for alkali cations with 4EGMC (Li$^+$ > Na$^+$ > K$^+$) (Figure S14). The kinetic studies were performed at ambient temperature with a ratio $[I]_0/[\mathrm{TBD}]_0/[\text{metal cation}]_0/[M]_0$ = 1:1:2:20, $[M]_0$ = 1 M in THF. The semilogarithmic plots of ROP of 4EGMC catalyzed by different cations with TBD showed the first-order polymerization, where the observed rate constant (k_{obs}) of the Li$^+$-mediated reaction is the highest among these cations, and Na$^+$ is the lowest (Li$^+$ k_{obs} 0.36 min^{-1} > K$^+$ k_{obs} 0.23 min^{-1} > Na$^+$ k_{obs} 0.16 min^{-1}, Figure 3c). Moreover, the polymerization of 4EGMC assisted by alkali cations revealed comparable molecular weights and dispersity characterized by ^{1}H NMR and SEC ($M_{n\ NMR}$ = 4.0−4.3 kg mol^{-1}, $M_{n\ SEC}$ = 5.8−6.3 kg mol^{-1}, and $Đ$ = 1.13−1.20, Table S3). In comparison with TBD-catalyzed polymerization (k_{obs} = 0.0013 min^{-1}), the addition of alkali cations shows extremely rapid kinetics with *ca.* 120−270 times over the TBD-catalyzed reaction.

We hypothesize that this cation-dependent k_{obs} could be correlated with the difference in binding energy (ΔE_c) between the macrocycle and alkali cations, where Li$^+$ is associated with a low ΔE_c over Na$^+$ and K$^+$. However, results of calculation revealed that ΔE_c of K$^+$/4EGMC was the lowest with an order Na$^+$ > Li$^+$ > K$^+$ (−5.4 kcal·mol^{-1} > −6.74 kcal·mol^{-1} > −10.9 kcal·mol^{-1}, Table S2). Sawamoto et al. reported that polyethylene glycol with functional chain ends can be tethered by certain alkali cations through the coordination affording pseudo-cyclic structures, which suggests the strong affinity of polyethylene glycol with alkali cations.[49] Therefore, we assume that the linear polycarbonate (P4EGMC) can also accommodate the cations. To simulate the binding energy for P4EGMC with cations, Job's plots were first performed to determine the stoichiometry of the interaction. The results revealed a 1:1 ratio complex for Na$^+$/P4EGMC and K$^+$/P4EGMC, while P4EGMC interacted with two Li$^+$ (i.e., [P4EGMC]/[Li$^+$] = 1:2) to form the complex (Figures S15−S18). The computational study demonstrated that the combination of P4EGMC and cations allowed the generation of thermodynamically favored complexes with the high binding energies of *ca.* −59.1 to −72.8 kcal·mol^{-1} (Table S2). This differs from the case of Na$^+$ and ethyleneoxy-substituted ester that the strong interaction between cyclic ester and Na$^+$ was observed.[50] Interestingly, the difference in relative binding energy between cyclic and corresponding linear formations corroborated the order of observed polymerization rate constant (k_{obs} Li$^+$ > K$^+$ > Na$^+$), where $\Delta\Delta E_{bc}$ of the Li$^+$-related complex is the lowest (53.7 kcal·mol^{-1}), while K$^+$ with a $\Delta\Delta E_{bc}$ value of 58 kcal·mol^{-1} and Na$^+$ with a $\Delta\Delta E_{bc}$ value of 66.1 kcal·mol^{-1} (Figure 4). We hypothesize that Li$^+$ can rapidly shuttle between the monomer and polymer during the polymerization process, in comparison to the K$^+$- and Na$^+$-catalyzed reaction, thereby leading to the fastest polymerization.

Cations depicted strong affinities to the open chain structures with high binding energies, which may slow the ROP and simultaneously promote the transesterification of the polymer chain. To verify the activity of the catalyst for transesterification, calculation for the step of nucleophilic addition to form a tetrahedral intermediate was performed (**Int1** to **Int2**). The results revealed that **TS1** for the cyclic structure presented a lower energy barrier than that of linear formation by *ca.* two times (6.7 kcal·mol^{-1} vs 15.8 kcal·mol^{-1}). In addition, **Int2** for linear carbonate is the thermodynamically disfavored (+5.86 kcal·mol^{-1}) which readily reverses to **Int1**, while the tetrahedral cyclic structure is relatively stable (−0.1 kcal·mol^{-1}). Thus, it is not surprising that the polymerization of 4EGMC assisted by alkali cations with a controlled manner

https://doi.org/10.1021/acs.macromol.3c01311
Macromolecules 2023, 56, 6790−6797

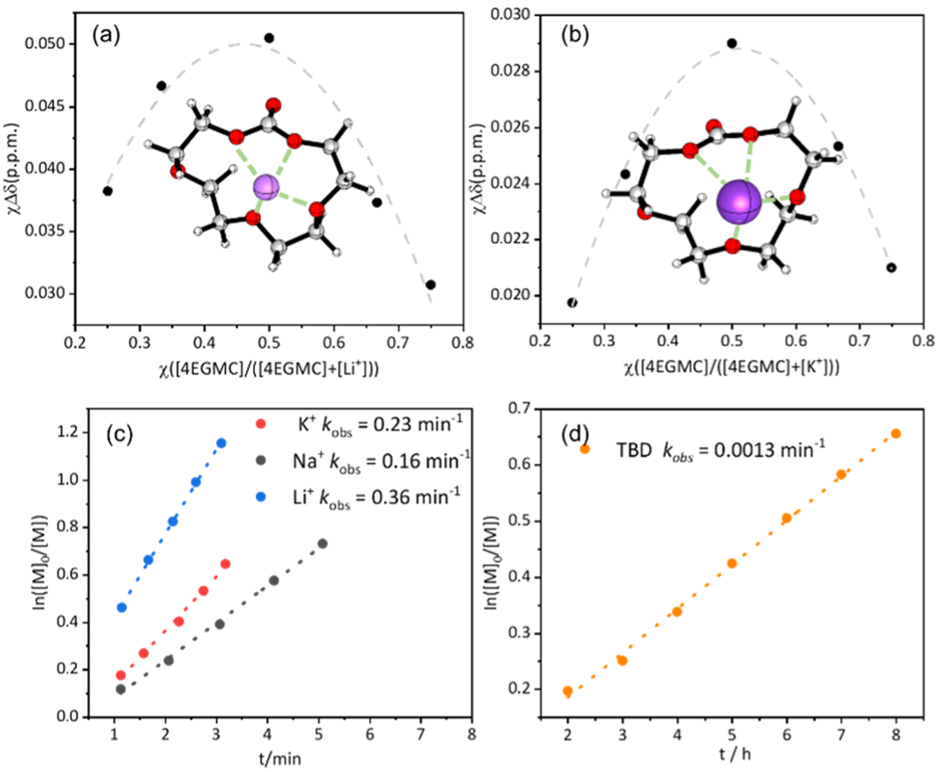


Figure 3. Job plots were obtained from [1]H NMR measurements of 4EGMC with $LiPF_6$ or KPF_6, $[4EGMC]_0 = 0.1$ M in CD_3CN; the structures were optimized at the B3LYP-D3/6-311+G(2d,p) level (a,b); (c) semilogarithmic kinetic plot of the ROP of 4EGMCs using TBD with different cations; (d) kinetic plot of the ROP of 4EGMCs catalyzed by TBD; experimental conditions: $[M]_0 = 1$ M, rt in THF, BnOH as the initiator, $[BnOH]_0/[cation]_0/[TBD]_0/[4EGMC]_0 = 1{:}0{:}1{:}20$, 1 mL THF, at ambient temperature; and $\ln([M]_0/[M]) = k_{obs}t$.

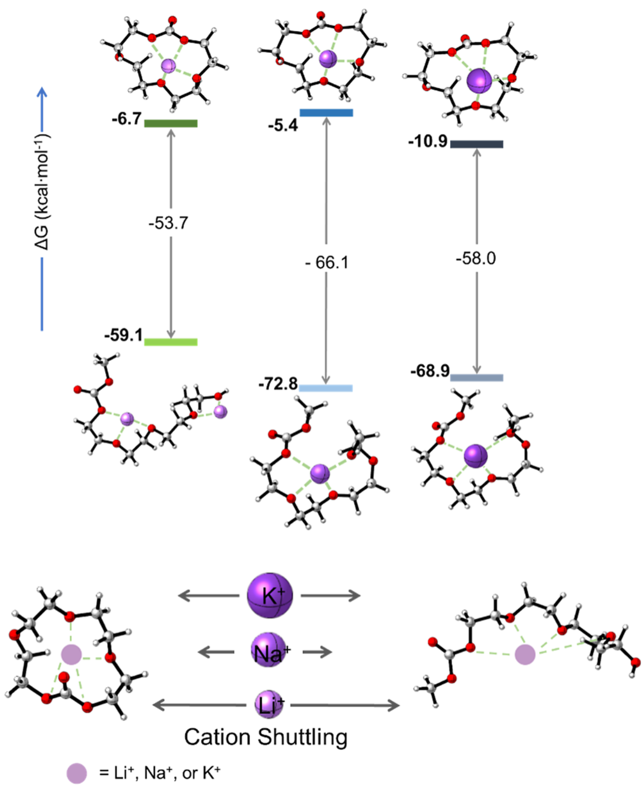


Figure 4. Energetic profiles with optimized structures for binding energies of cyclic or linear formation carbonate with different cations at the B3LYP/def2-TZVP(PCM, solvent = THF)//B3LYP-D3/6-311+G(2d,p) level.

is associated with fast kinetics, albeit the strong affinity between P4EGMC and cations (Figure 5).

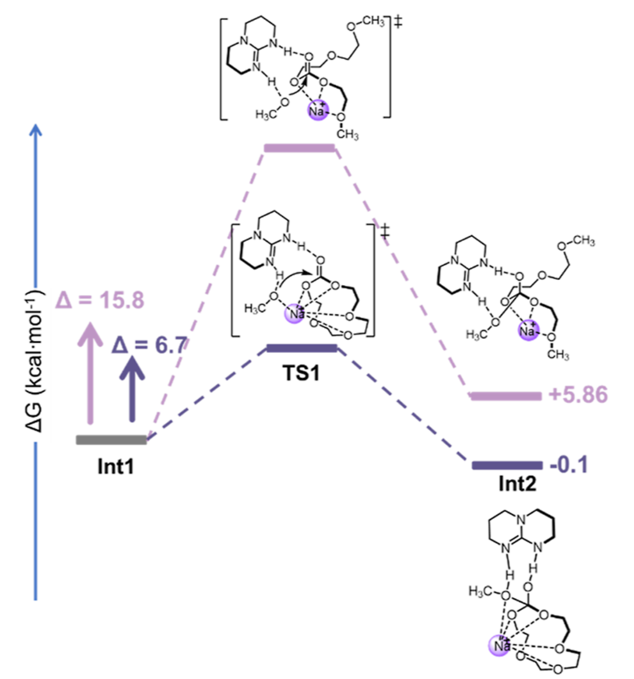


Figure 5. Energetic profiles for the nucleophilic addition of methanol to cyclic or linear carbonate at the B3LYP/aug-cc-PVTZ(PCM, solvent = THF)//B3LYP-D3/6-311+G(2d,p) level.

https://doi.org/10.1021/acs.macromol.3c01311
Macromolecules 2023, 56, 6790−6797

CONCLUSIONS

A fast kinetics of ROP of macrocyclic carbonate was achieved through a catalytic combination of TBD and alkali cation at ambient temperature. The thermodynamic study, supported by both experiments and DFT calculations, revealed the sodium cation coordinated with MC, leading to a constrained ring, thereby changing the thermodynamic-driven force for polymerization from entropy- to enthalpy-driven. Moreover, the DFT-calculated reaction demonstrates that the sodium cation is the crucial catalyst for the polymerization as the coordination of Na^+ with MC and the initiator affording thermodynamically favored intermediates and transition states. Surprisingly, the order in the catalytic activities of Li^+, Na^+, and K^+ was not associated with the corresponding binding energy to MC but was a result of the ability of the cation to shuttle between MC and the polymer chain (i.e., the relative binding energy).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c01311.

General method, synthesis details, ^{1}H NMR and ^{13}C NMR spectra, SEC curves, reaction kinetics, and computational details (PDF)

Crystallographic data of complex 4EGMC (CIF)

AUTHOR INFORMATION

Corresponding Authors

Jin Huang − *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China;* orcid.org/0000-0002-5571-5017; Email: jinhuang@njtech.edu.cn

Lili Zhao − *Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China;* orcid.org/0000-0003-2580-6919; Email: ias_llzhao@njtech.edu.cn

Kai Guo − *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China;* orcid.org/0000-0002-0013-3263; Email: guok@njtech.edu.cn

Authors

Yuanyuan Qu − *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Junyuan Hu − *Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China*

Fengzhen Guo − *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Dong Ji − *Institute of Nanjing Advanced Biomaterials & Processing Equipment, Nanjing 211299, China*

Yuguang Li − *Institute of Nanjing Advanced Biomaterials & Processing Equipment, Nanjing 211299, China*

Zhenjiang Li − *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China;* orcid.org/0000-0002-1100-7297

Yunsheng Xu − *School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.3c01311

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.H. thanks the China Postdoc Council (OCPC) for the financial support of the Postdoctoral International Exchange Program (YJ20210095). The authors thank the financial support from the National Natural Science Foundation of China (22078150 and 21973044), the National Key R&D Program of China (2021YFC2101903), the Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM); the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Jiangsu Synergetic Innovation Center for Advanced Bio-Manufacture (XTB2201), the Top-Notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), the Jiangsu Province Industrial Prospects and Key Core Technologies-Competitive Projects (BE2021083), and the Natural Science Foundation of Jiangsu Province (BK20211587). We also appreciated the high-performance center of Nanjing Tech University for supporting the computational resources.

REFERENCES

(1) Gnanou, Y. Epilogue: Sorting, Depolymerizing, Recycling Polymers: The Long Road to a Circular Plastics Economy. In *Macromolecular Engineering*; Hadjichristidis, N., Gnanou, Y., Matyjaszewski, K., Muthukumar, M., Eds.; Wiley, 2022; pp 1−30.

(2) Worch, J. C.; Dove, A. P. 100th Anniversary of Macromolecular Science Viewpoint: Toward Catalytic Chemical Recycling of Waste (and Future) Plastics. *ACS Macro Lett.* **2020**, *9* (11), 1494−1506.

(3) Fan, H.-Z.; Yang, X.; Chen, J.-H.; Tu, Y.-M.; Cai, Z.; Zhu, J.-B. Advancing the Development of Recyclable Aromatic Polyesters by Functionalization and Stereocomplexation. *Angew. Chem., Int. Ed.* **2022**, *61* (15), No. e202117639.

(4) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. Organocatalytic Ring-Opening Polymerization. *Chem. Rev.* **2007**, *107* (12), 5813−5840.

(5) Nuyken, O.; Pask, S. D. Ring-Opening Polymerization—An Introductory Review. *Polymers* **2013**, *5* (2), 361−403.

(6) Ottou, W. N.; Sardon, H.; Mecerreyes, D.; Vignolle, J.; Taton, D. Update and challenges in organo-mediated polymerization reactions. *Prog. Polym. Sci.* **2016**, *56*, 64−115.

(7) Mespouille, L.; Coulembier, O.; Kawalec, M.; Dove, A. P.; Dubois, P. Implementation of metal-free ring-opening polymerization in the preparation of aliphatic polycarbonate materials. *Prog. Polym. Sci.* **2014**, *39* (6), 1144−1164.

(8) Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M. Catalysis as an Enabling Science for Sustainable Polymers. *Chem. Rev.* **2018**, *118* (2), 839−885.

(9) Lin, B.; Waymouth, R. M. Urea Anions: Simple, Fast, and Selective Catalysts for Ring-Opening Polymerizations. *J. Am. Chem. Soc.* **2017**, *139* (4), 1645−1652.

(10) Hong, M.; Chen, E. Y. X. Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of γ-butyrolactone. *Nat. Chem.* **2016**, *8* (1), 42−49.

(11) Xia, X.; Gao, T.; Li, F.; Suzuki, R.; Isono, T.; Satoh, T. Sequential Polymerization from Complex Monomer Mixtures: Access to Multiblock Copolymers with Adjustable Sequence, Topology, and Gradient Strength. *Macromolecules* **2023**, *56* (1), 92−103.

(12) Guo, Y.-T.; Shi, C.; Du, T.-Y.; Cheng, X.-Y.; Du, F.-S.; Li, Z.-C. Closed-Loop Recyclable Aliphatic Poly(ester-amide)s with Tunable Mechanical Properties. *Macromolecules* **2022**, *55* (10), 4000−4010.

(13) Shi, J.; Liu, Z.; Zhao, N.; Liu, S.; Li, Z. Controlled Ring-Opening Polymerization of Hexamethylcyclotrisiloxane Catalyzed by Trisphosphazene Organobase to Well-Defined Poly-(dimethylsiloxane)s. *Macromolecules* **2022**, *55* (7), 2844−2853.

(14) Zhang, X.; Jones, G. O.; Hedrick, J. L.; Waymouth, R. M. Fast and selective ring-opening polymerizations by alkoxides and thioureas. *Nat. Chem.* **2016**, *8* (11), 1047−1053.

(15) Hong, M.; Chen, J.; Chen, E. Y. X. Polymerization of Polar Monomers Mediated by Main-Group Lewis Acid-Base Pairs. *Chem. Rev.* **2018**, *118* (20), 10551−10616.

(16) Yang, J.-C.; Yang, J.; Li, W.-B.; Lu, X.-B.; Liu, Y. Carbonylative Polymerization of Epoxides Mediated by Tri-metallic Complexes: A Dual Catalysis Strategy for Synthesis of Biodegradable Polyhydroxyalkanoates. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202116208.

(17) Yang, R.; Xu, G.; Lv, C.; Dong, B.; Zhou, L.; Wang, Q. Zn(HMDS)2 as a Versatile Transesterification Catalyst for Polyesters Synthesis and Degradation toward a Circular Materials Economy Approach. *ACS Sustainable Chem. Eng.* **2020**, *8* (50), 18347−18353.

(18) Zhou, Y.; Gao, Z.; Hu, C.; Meng, S.; Duan, R.; Sun, Z.; Pang, X. Facile Synthesis of Gradient Polycarbonate-Polyester Terpolymers from Monomer Mixtures Mediated by an Asymmetric Chromium Complex. *Macromolecules* **2022**, *55* (22), 9951−9959.

(19) D'Alterio, M. C.; D'Auria, I.; Gaeta, L.; Tedesco, C.; Brenna, S.; Pellecchia, C. Are Well Performing Catalysts for the Ring Opening Polymerization of l-Lactide under Mild Laboratory Conditions Suitable for the Industrial Process? The Case of New Highly Active Zn(II) Catalysts. *Macromolecules* **2022**, *55* (12), 5115−5122.

(20) Yan, Q.; Li, C.; Yan, T.; Shen, Y.; Li, Z. Chemically Recyclable Thermoplastic Polyurethane Elastomers via a Cascade Ring-Opening and Step-Growth Polymerization Strategy from Bio-renewable δ-Caprolactone. *Macromolecules* **2022**, *55* (10), 3860−3868.

(21) Ivin, K. J.; Léonard, J. The effect of polymer concentration on the equilibrium monomer concentration for the anionic polymerization of α-methylstyrene in tetrahydrofuran. *Eur. Polym. J.* **1970**, *6* (2), 331−341.

(22) Léonard, J.; Bui, V. T. Solvent effect on the equilibrium polymerization of α-methylstyrene. *Polymer* **1987**, *28* (6), 1041−1045.

(23) Bui, V. T.; Léonard, J. Interaction parameters and the equilibrium cationic polymerization of tetrahydrofuran in benzene. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82* (3), 899−908.

(24) MacDonald, J. P.; Shaver, M. P. An aromatic/aliphatic polyester prepared via ring-opening polymerisation and its remarkably selective and cyclable depolymerisation to monomer. *Polym. Chem.* **2016**, *7* (3), 553−559.

(25) Olsén, P.; Undin, J.; Odelius, K.; Keul, H.; Albertsson, A.-C. Switching from Controlled Ring-Opening Polymerization (cROP) to Controlled Ring-Closing Depolymerization (cRCDP) by Adjusting the Reaction Parameters That Determine the Ceiling Temperature. *Biomacromolecules* **2016**, *17* (12), 3995−4002.

(26) Cederholm, L.; Wohlert, J.; Olsén, P.; Hakkarainen, M.; Odelius, K. "Like Recycles Like": Selective Ring-Closing Depolymerization of Poly(L-Lactic Acid) to L-Lactide. *Angew. Chem., Int. Ed.* **2022**, *61* (33), No. e202204531.

(27) Huang, J.; Yan, R.; Ni, Y.; Shi, N.; Li, Z.; Ma, C.; Guo, K. Cyclic Polycarbonates by N-Heterocyclic Carbene-Mediated Ring-Expansion Polymerization and Their Selective Depolymerization to Monomers. *ACS Sustainable Chem. Eng.* **2022**, *10* (46), 15007−15016.

(28) Huang, J.; Olsén, P.; Svensson Grape, E.; Inge, A. K.; Odelius, K. Simple Approach to Macrocyclic Carbonates with Fast Polymerization Rates and Their Polymer-to-Monomer Regeneration. *Macromolecules* **2022**, *55* (2), 608−614.

(29) Hori, K.; Yamada, H.; Yamabe, T. Theoretical study on the nature of the interaction between crown ethers and alkali cations: Relation of interaction energy and ion selectivity. *Tetrahedron* **1983**, *39* (1), 67−73.

(30) Yoshio, M.; Noguchi, H. Crown Ethers for Chemical Analysis: A Review. *Anal. Lett.* **1982**, *15* (15), 1197−1276.

(31) Moins, S.; Henoumont, C.; De Roover, Q.; Laurent, S.; De Winter, J.; Coulembier, O. Accelerating effect of crown ethers on the lactide polymerization catalysed by potassium acetate. *Catal. Sci. Technol.* **2021**, *11* (13), 4387−4391.

(32) Wang, T.; Bradshaw, J. S.; Izatt, R. M. Applications of NMR spectral techniques for the study of macrocycle host-organic guest interactions. A short review. *J. Heterocycl. Chem.* **1994**, *31* (5), 1097−1114.

(33) McMurry, J. E. *Fundamentals of Organic Chemistry*; Cengage Learning, 2010.

(34) Mayfield, H. G.; Bull, W. E. Co-ordinating tendencies of the hexafluorophosphate ion. *J. Chem. Soc. A* **1971**, No. 0, 2279−2281.

(35) Johann, C.; Kilz, P. Utilization Of Size-Exclusion Chromatography. *Polymer Analysis and Characterization: Proceedings of the International Symposium on Polymer Analysis and Characterization*; John Wiley & Sons, 1991; p 111.

(36) Gerle, M.; Fischer, K.; Roos, S.; Müller, A. H. E.; Schmidt, M.; Sheiko, S. S.; Prokhorova, S.; Möller, M. Main chain conformation and anomalous elution behavior of cylindrical brushes as revealed by GPC/MALLS, light scattering, and SFM. *Macromolecules* **1999**, *32* (8), 2629−2637.

(37) Al-Sabagh, A. M.; Yehia, F. Z.; Eissa, A. M. F.; Moustafa, M. E.; Eshaq, G.; Rabie, A. M.; ElMetwally, A. E. Cu- and Zn-acetate-containing ionic liquids as catalysts for the glycolysis of poly(ethylene terephthalate). *Polym. Degrad. Stab.* **2014**, *110*, 364−377.

(38) Podzimek, S.; Vlcek, T.; Johann, C. Characterization of branched polymers by size exclusion chromatography coupled with multiangle light scattering detector. I. Size exclusion chromatography elution behavior of branched polymers. *J. Appl. Polym. Sci.* **2001**, *81* (7), 1588−1594.

(39) Gaborieau, M.; Castignolles, P. Size-exclusion chromatography (SEC) of branched polymers and polysaccharides. *Anal. Bioanal. Chem.* **2011**, *399* (4), 1413−1423.

(40) Tan, S. Y.; Ang, C. Y.; Zhao, Y. 5.17—Smart Therapeutics Achieved via Host-Guest Assemblies. In *Comprehensive Supramolecular Chemistry II*; Atwood, J. L., Ed.; Elsevier: Oxford, 2017; pp 391−420.

(41) Pedersen, C. J. The Discovery of Crown Ethers (Noble Lecture). *Angew Chem. Int. Ed.* **1988**, *27* (8), 1021−1027.

(42) Steed, J. W. First- and second-sphere coordination chemistry of alkali metal crown ether complexes. *Coord. Chem. Rev.* **2001**, *215* (1), 171−221.

(43) Live, D.; Chan, S. I. Nuclear magnetic resonance study of the solution structures of some crown ethers and their cation complexes. *J. Am. Chem. Soc.* **1976**, *98* (13), 3769−3778.

(44) Olsén, P.; Odelius, K.; Albertsson, A.-C. Thermodynamic Presynthetic Considerations for Ring-Opening Polymerization. *Biomacromolecules* **2016**, *17* (3), 699−709.

(45) Hodge, P. Entropically Driven Ring-Opening Polymerization of Strainless Organic Macrocycles. *Chem. Rev.* **2014**, *114* (4), 2278−2312.

(46) Gregory, G. L.; Kociok-Köhn, G.; Buchard, A. Polymers from sugars and CO2: ring-opening polymerisation and copolymerisation of cyclic carbonates derived from 2-deoxy-d-ribose. *Polym. Chem.* **2017**, *8* (13), 2093−2104.

(47) Gregory, G. L.; Jenisch, L. M.; Charles, B.; Kociok-Köhn, G.; Buchard, A. Polymers from Sugars and CO2: Synthesis and Polymerization of a d-Mannose-Based Cyclic Carbonate. *Macromolecules* **2016**, *49* (19), 7165−7169.

https://doi.org/10.1021/acs.macromol.3c01311
Macromolecules 2023, 56, 6790−6797

(48) Lu, T.; Chen, Q. Interaction Region Indicator: A Simple Real Space Function Clearly Revealing Both Chemical Bonds and Weak Interactions**. *Chem.: Methods* **2021**, *1* (5), 231−239.
(49) Terashima, T.; Kawabe, M.; Miyabara, Y.; Yoda, H.; Sawamoto, M. Polymeric pseudo-crown ether for cation recognition via cation template-assisted cyclopolymerization. *Nat. Commun.* **2013**, *4* (1), 2321.
(50) Hu, Z.; Cao, X.; Zhang, X.; Wu, B.; Luo, W.; Huang, H.; Li, L.; Chen, Y. Catalytically Controlled Ring-Opening Polymerization of 2-Oxo-15-crown-5 for Degradable and Recyclable PEG-Like Polyesters. *ACS Macro Lett.* **2022**, *11* (6), 792−798.

https://doi.org/10.1021/acs.macromol.3c01311
Macromolecules 2023, 56, 6790−6797