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# Thermodynamics of Aromatic Cyclic Ester Polymerization in Bulk

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**Abstract** We present here the thermodynamic investigation of *in situ* cascade polycondensation-coupling ring-opening polymerization (PROP) for three cyclic aromatic ester monomers, *i.e.*, cyclic oligo(2-methyl-1,3-propylene terephthalate)s (COMPTs), cyclic oligo(neopentylene terephthalate)s (CONTs) and cyclic oligo(2-methyl-2-propyl-1,3-propylene terephthalate)s (COMPPTs). The equilibrium monomer to polymer weight ratio in bulk at different polymerization temperatures for each monomer was estimated by the size exclusion chromatography (SEC), and the thermodynamic parameters were estimated by Dainton equation. Quite different from the thermodynamics of aliphatic lactones polymerization, which is an exothermic process with entropy reduction, our results showed the polymerization thermodynamics for three cyclic aromatic ester monomers was a weak exothermic process with slight entropy increment, *i.e.*, a both enthalpy and entropy driving process. Among them, CONTs showed the largest value of enthalpy change, due to its symmetric dimethyl substitution on  $\beta$ -position of propandiol segments.

**Keywords** Lactone; Polyester; Polycondensation-coupling ring-opening polymerization; Thermodynamic parameters

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## INTRODUCTION

Ring-opening polymerization (ROP) of lactones or lactides is an efficient way for the synthesis of aliphatic polyesters. For example, poly( $\beta$ -propiolactone) (PPL), polycaprolactone (PCL), poly(1,4-dioxan-2-one) (PPDX) and polylactide (PLA) are synthesized *via* ROP from their corresponding lactone or lactide monomers.<sup>[1–5]</sup> Recently, poly(ethylene brassylate) was reported to be synthesized from ethylene brassylate *via* ROP by the pioneering work of Mecerreyes *et al.*<sup>[6,7]</sup> Thermodynamic studies show that the ROP of these aliphatic cyclic esters is an enthalpy driving process together with the entropy reduction, as there is ring strain in these cyclic esters.<sup>[8,9]</sup> The polyesters synthesized can achieve high molecular weights and are important types of the biocompatible and degradable polymers.<sup>[10,11]</sup>

On the other hand, aromatic polyesters are typically synthesized by condensation polymerization with excellent physical and chemical properties, including high melting points, outstanding hydrolysis resistance, *etc.*<sup>[12,13]</sup> Brunelle *et al.* reported the synthesis of cyclic oligo(aromatic ester)s *via* pseudo-high dilution condensation of diols with terephthaloyl chloride.<sup>[14–16]</sup> ROP of these monomers is efficient and poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) with high molecular weights can be easily achieved.<sup>[17–19]</sup> Recently, the corresponding ROP synthesis of poly(ethylene 2,5-furandicarboxylate) (PEF) and

poly(butylene 2,5-furandicarboxylate) (PBF) from their cyclic oligoesters has also been thoroughly studied<sup>[20–22]</sup> due to their excellent barrier properties, which is suitable for package materials.<sup>[23,24]</sup> However, to our knowledge, the thermodynamic polymerization parameters for aromatic cyclic esters have not been studied because of the poor solubility of cyclic oligoesters and corresponding polyesters.

We recently reported an *in situ* cascade polycondensation-coupling ring-opening polymerization (PROP) method for the synthesis of polyesters and poly(ether ester) multiblock copolymers.<sup>[25–28]</sup> The polymerization mechanism was proven by the study on a series of aromatic cyclic oligo(1,3-propylene terephthalate) analogues with alkyl chain substitution on  $\beta$ -position of 1,3-propanediol, *i.e.* cyclic oligo(2-methyl-1,3-propylene terephthalate)s (COMPTs), cyclic oligo(neopentylene terephthalate)s (CONTs), and cyclic oligo(2-methyl-2-propyl-1,3-propylene terephthalate)s (COMPPTs). Corresponding aromatic polyesters with relatively high molecular weights, *i.e.* poly(2-methyl-1,3-propylene terephthalate) (PMPT), poly(neopentylene terephthalate) (PNT) and, poly(2-methyl-2-propyl-1,3-propylene terephthalate) (PMPPT), can be synthesized from the monomers *via* PROP, which are difficult to be obtained by traditional condensation polymerization method due to the introduction of bulky substituted alkyl chains. Interestingly, the introduction of side chains significantly improves the solubility of cyclic oligoester monomers and polyesters, and they can be dissolved in common solvents like chloroform (CHCl<sub>3</sub>) and tetrahydrofuran (THF) at room temperature. This provides a facile method to calculate the monomer conversion *via* size exclusion chromatography (SEC), and enables the estima-

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tion of thermodynamic parameters.

In this paper, we would like to study the thermodynamic parameters for the polymerization of above mentioned three aromatic cyclic esters, COMPTs, CONTs, and COMPPTs. The obtained enthalpy and entropy change during polymerization from these aromatic cyclic esters and the driving force will be compared with those for the traditional aliphatic lactones to see the difference.

## EXPERIMENTAL

### Instruments

Size exclusion chromatography (SEC) analysis was performed on a modular system comprising a Waters 1515 pump, a 717 plus autosampler, and a 2410 refractive index detector. Separations were achieved using two PL Mixed-C columns (7.5 mm × 300 mm, 5 μm bead size, 0.2–2000 kDa), calibrated with 9 narrow distribution polystyrene standards with a molecular weight range from 0.47 kDa to 177 kDa. All samples (2 mg·mL<sup>-1</sup>) were passed through 0.45 μm PTFE filter before analysis and THF was used as mobile phase at a flow rate of 1.0 mL·min<sup>-1</sup> at 35 °C.

### Synthesis of Polyesters

PMPT, PNT, and PMPPT polyesters were synthesized *via* PROP method according to our previously reported process, using cyclic oligoesters as monomer and corresponding diols as initiator.<sup>[27]</sup> Due to the high melting temperatures of aromatic cyclic oligoesters (about 213 °C for COMPTs, 268 °C for CONTs, and 224 °C for COMPPTs, respectively), the bulk polymerization temperatures were kept slightly higher than the cyclic monomers' melting temperature. The polymerization temperature can be lowered greatly when using solution polymerization techniques, according to previous studies.<sup>[29,30]</sup> To achieve thermodynamic equilibrium concentration, polymerization was carried out at different temperatures for prolonged time until the elution percentage of monomer to polymer detected by SEC was constant.

### Density Measurements

The density of polyesters was determined by the suspension method. Since polyesters are not soluble in *n*-hexane ( $\rho = 0.659 \text{ g}\cdot\text{cm}^{-3}$ ) and carbon tetrachloride ( $\rho = 1.595 \text{ g}\cdot\text{cm}^{-3}$ ), the two mutually mixable solvents were selected and their volume ratio was adjusted to make the test samples suspend in the solvent mixture. At this point, the density of the liquid is equal to the density of sample.

## RESULTS AND DISCUSSION

In a typical ROP system, there is an equilibrium concentration between the polyester and the monomer. Scheme 1 shows the dynamic equation between our aromatic cyclic oligoesters and polyesters at their thermodynamic equilibrium state. In this case, assuming the concentration of growing chain  $P_n$  is equal to  $P_{n+2}$ , the enthalpy change ( $\Delta H_P$ ), entropy change ( $\Delta S_P$ ) and monomer concentration at equilibrium ( $[M]_{eq}$ ) can be correlated by the Gibbs free energy ( $\Delta G_P$ ):<sup>[31]</sup>

$$\Delta G_P = \Delta H_P - T\Delta S_P = RT \ln[M]_{eq} \quad (1)$$

where  $R$  is gas constant,  $T$  is the absolute temperature. Eq. (1) can be converted to the known Dainton's equation (Eq. 2):<sup>[32,33]</sup>

$$\ln[M]_{eq} = \frac{\Delta H_P}{RT} - \frac{\Delta S_P}{R} \quad (2)$$

In the bulk melt polymerization process, the monomer concentration at equilibrium ( $[M]_{eq}$ ) can be obtained by Eq. (3):

$$[M]_{eq} = \frac{n_M}{V} \approx \frac{\left(\frac{m_M}{M_M}\right)}{\left(\frac{m_P + m_M}{\rho_P}\right)} = \frac{m_M}{m_P + m_M} \times \frac{\rho_P}{M_M} \quad (3)$$

where  $n_M$  is the mole of monomer,  $V$  is the volume of the total polymer,  $m_M$  is the weight of the monomer,  $m_P$  is the weight of polymer,  $M_M$  is the molar mass of the monomer ( $\text{g}\cdot\text{mol}^{-1}$ ),  $\rho_P$  is the density of the polymer (in  $\text{g}\cdot\text{dm}^{-3}$ ). Since the monomer conversion is very high ( $> 95\%$ ), the density of melt is assumed to be the same as the density of polyester.

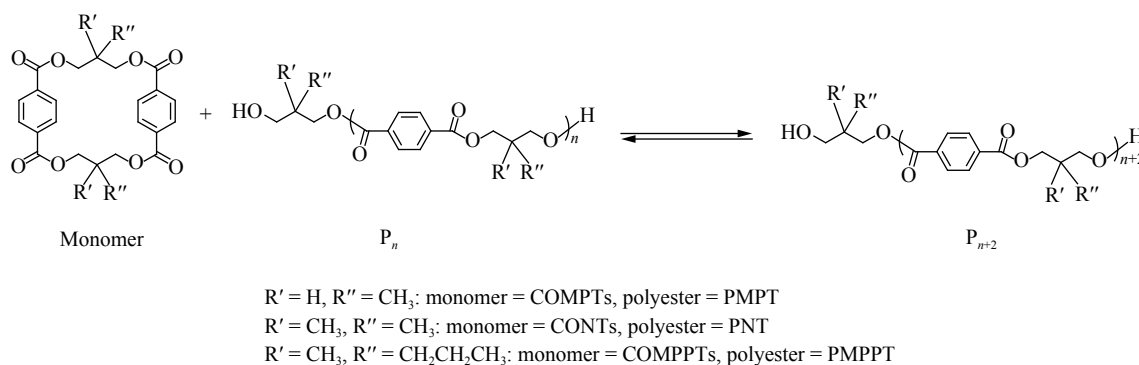
Combination of Eqs. (2) and (3) leads to Eqs. (4) and (5):

$$R \ln \alpha = \frac{\Delta H_P}{T} - \Delta S_P - R \ln \frac{\rho_P}{M_M} \quad (4)$$

$$\alpha = \frac{m_M}{m_P + m_M} = 1 - \text{conv.} \quad (5)$$

where  $\alpha$  is the monomer weight ratio in equilibrium polymer melt, conv. is the conversion of monomer. By plotting  $R \ln \alpha$  versus  $1/T$ , the value of  $\Delta H_P$  can be obtained from slope, while  $\Delta S_P$  from the intercept.

The value of  $\alpha$  can be estimated from the SEC characterization by the corrected area percentage of corresponding



**Scheme 1** The corresponding equilibrium state between aromatic cyclic oligoesters and polyesters

monomer to total monomer and polymer. Since usually the refractive index detector is used for the signal acquisition in SEC measurements, while aromatic polyesters and their cyclic oligoesters have different specific refractive index increment ( $dn/dc$ ) as reported by Burch *et al.*,<sup>[34]</sup> the area obtained by SEC must be calibrated. The calibration factors ( $R_f$ ) can be obtained from the area ratio of corresponding polyesters ( $A_p$ ) and cyclic oligomers ( $A_{CO}$ ) at same normalized concentration:  $R_f = A_p/A_{CO}$ . The measured calibration factor for PMPT, PNT, and PMPPT is 1.059, 1.056 and 1.115.<sup>[27]</sup>

To ensure polymer and monomer concentration achieving the equilibrium state, the polymerization melts were taken out after each 30 min until the conversion of aromatic lactone reached a constant value. Fig. 1(a) shows the SEC curves of polymer melts at equilibrium state for the system of PMPT and COMPTs at temperature of 250, 260, 270, and 280 °C, with polymerization time of 6, 5, 3, and 3 h, respectively. The calibrated monomer weight ratio ( $\alpha$ ) is 0.03627, 0.03637, 0.03656 and 0.03673 at 250, 260, 270, and 280 °C, respectively.

The thermodynamic plot is presented in Fig. 1(b). The enthalpy change ( $\Delta H_p$ ) obtained from the slope is  $-1.07 \text{ kJ} \cdot \text{mol}^{-1}$ , indicating that the polymerization of COMPTs is a slight exothermic process. The entropy change ( $\Delta S_p$ ) during polymerization calculated from intercept is  $17.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , in-

dicating the polymerization of these aromatic cyclic oligoesters is a both enthalpy and entropy driving process.

It should be noted that for the deduction of entropy change, the molecular weight used for cyclic lactone monomer is that from dimer, since usually cyclic dimer is the most stable state for these cyclic oligoesters. This is supported by the SEC results, where the peak position for cyclic monomers is the same as that for dimer, and the peaks for other cyclic oligomers are neglectable.

On the other hand, since the density at high temperatures is hard to be measured, the density of PMPT at room temperature is used instead, which is  $1224 \text{ g} \cdot \text{dm}^{-3}$ . This introduces small error for the system, as solid's and liquid's densities do not change much as a factor of temperature, and a density change from  $1200 \text{ g} \cdot \text{dm}^{-3}$  to  $1100 \text{ g} \cdot \text{dm}^{-3}$  provides about  $1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  to the entropy change of system.

Since the melting temperature of CONTs is about 268 °C, quite higher than that for COMPTs, the polymerization for CONTs was carried at 280 °C and higher. At these conditions, the equilibrium polymerization state can be reached in shorter time. Fig. 2(a) shows the SEC curves of CONTs and PNT at equilibrium polymerization state, at temperatures of 280, 290, 300, and 310 °C, with polymerization time of 2, 2, 1.5, and 1.5 h, respectively. The calibrated monomer weight ratio  $\alpha$ , is 0.03061, 0.03166, 0.03141, and 0.03172.

Fig. 2(b) shows the thermodynamic plot of CONTs and

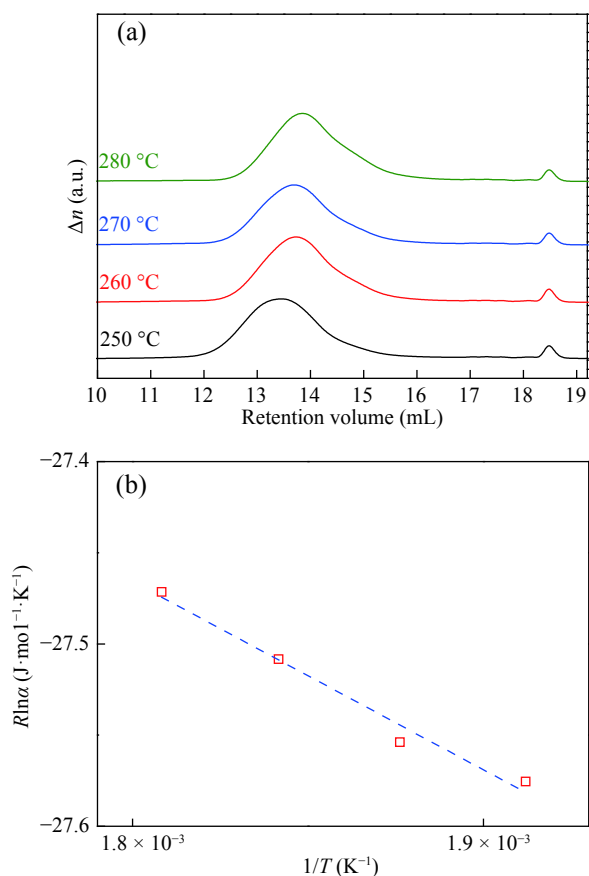


**Fig. 1** (a) SEC curves of COMPTs and PMPT at thermodynamic equilibrium state polymerized at different temperatures (250, 260, 270, and 280 °C); (b) thermodynamic plot for COMPTs and PMPT system

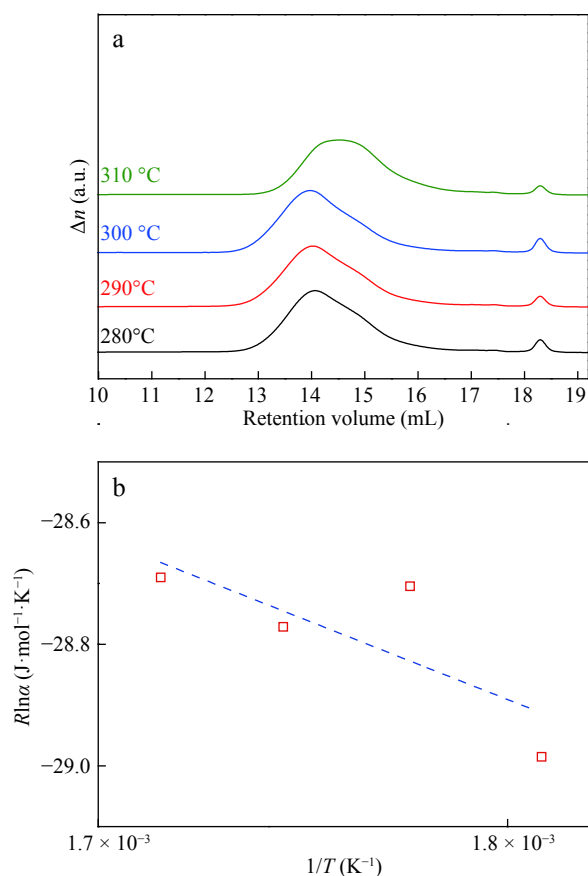


**Fig. 2** (a) SEC curves of CONTs and PNT at thermodynamic equilibrium state polymerized at different temperatures (280, 290, 300, and 310 °C); (b) thermodynamic plot for CONTs and PNT system

PNT. The measured enthalpy change is  $-2.67 \text{ kJ}\cdot\text{mol}^{-1}$ , again an exothermic polymerization process. From the intercept and measured density of PNT at room temperature ( $1199 \text{ g}\cdot\text{dm}^{-3}$ ), the deduced entropy change is  $16.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Similar to COMPTs, the system is a both enthalpy and entropy driving process.

The SEC curves of equilibrium polymerization state from COMPPTs and PMPPT are presented in Fig. 3(a), at temperatures of 250, 260, 270, and 280 °C, with polymerization time of 6, 6, 4, and 4 h, and calibrated monomer weight ratio of 0.09269, 0.09357, 0.09108 and 0.09487, respectively. The equilibrium monomer ratio in this system is larger than the previous two due to the long alkyl chains introduced, which hinders the flexibility of main-chain and reduces the entropy change during polymerization. This is supported by the thermodynamic plot in Fig. 3(b), where the obtained enthalpy change is  $-1.06 \text{ kJ}\cdot\text{mol}^{-1}$  and the entropy change of  $10.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  (polymer density is  $1188 \text{ g}\cdot\text{dm}^{-3}$ ). The entropy change of the system is smaller than the previous two systems.

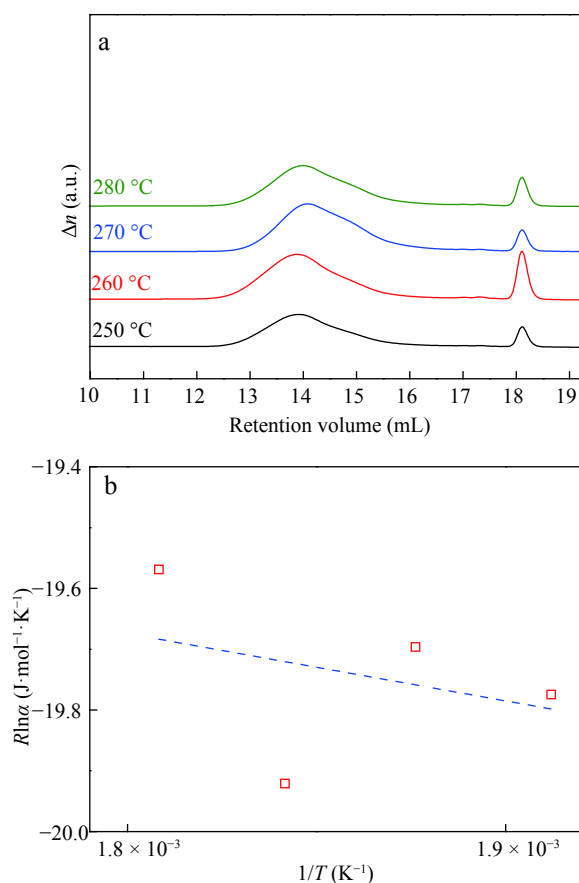


**Fig. 3** (a) SEC curves of COMPPTs and PMPPT at thermodynamic equilibrium state polymerized at different temperatures (250, 260, 270, and 280 °C); (b) thermodynamic plot for COMPPTs and PMPPT system

It should be noted that at equilibrium polymerization state of three aromatic cyclic oligoesters, the molecular weights of corresponding polyesters drop slightly with the increment of polymerization temperature (from 46 kDa at 250 °C to 30 kDa at 280 °C for PMPTs, 29 kDa at 280 °C to 18 kDa at

310 °C for PNTs, and 29 kDa at 250 °C to 28 kDa at 280 °C for PMPPTs, respectively). This is due to the side reactions in polyesters at such high polymerization temperatures,<sup>[35]</sup> as supported by the change of polyesters' colour from pale yellow to brown with increasing polymerization temperature. Because of the trans-esterification reactions during polymerization, the side reactions result in lower polyester molecular weights, yet have little effect on the polyester/cyclic monomer equilibrium ratio.

The obtained thermodynamic parameters for our aromatic cyclic oligoester systems are quite different from those of aliphatic lactones. Typically, the ROP of aliphatic lactones is an enthalpy driving process, *i.e.*, the enthalpy change is quite large ( $-\Delta H_p$  more than  $10 \text{ kJ}\cdot\text{mol}^{-1}$ ) while the entropy change ( $\Delta S_p$ ) is negative. For our aromatic system, the absolute value of enthalpy change is only few  $\text{kJ}\cdot\text{mol}^{-1}$ , smaller than that of aliphatic systems, yet the entropy change is positive. These results suggest that the ring strain in the aromatic cyclic oligoesters is smaller than those in aliphatic systems due to the large ring size of cyclic oligoesters. On the other hand, with cyclic topology and rigid phenyl groups, some conformational isomers are hard to be achieved in those aromatic cyclic oligoesters, which results in the increment of entropy change after polymerization. As a result, the polymerization of aromatic cyclic monomers is a both enthalpy and entropy driving process. As we know, such kind of polymerization thermodynamics has not been reported.

## CONCLUSIONS

In summary, the polymerization thermodynamics of three aromatic cyclic oligoesters, COMPTs, CONTs, and COMPPTs, has been investigated at their dynamic equilibrium state. Our results show that these are both enthalpy and entropy driving systems, with the enthalpy change value of  $-(1-2) \text{ kJ}\cdot\text{mol}^{-1}$  and entropy change value of  $10-20 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Such kind of thermodynamics is quite different from the polymerization of aliphatic lactones, where the entropy change is negative. Among the three aromatic cyclic oligoesters, CONTs show the largest absolute enthalpy change, while COMPPTs show the smallest entropy change during polymerization. Our results reveal the different polymerization thermodynamics between aromatic and aliphatic lactones, and should be useful for the design and synthesis of aromatic polyesters.

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## REFERENCES

- 1 Zhao, W.; Cui, D.; Liu, X.; Chen, X. Facile synthesis of hydroxyl-ended, highly stereoregular, star-shaped poly(lactide)

- from immortal ROP of rac-lactide and kinetics study. *Macromolecules* **2010**, *43*, 6678–6684.
- 2 Pascual, A.; Sardón, H.; Ruipérez, F.; Gracia, R.; Sudam, P.; Veloso, A.; Mecerreyes, D. Experimental and computational studies of ring-opening polymerization of ethylene brassylate macrolactone and copolymerization with  $\epsilon$ -caprolactone and TBD-guanidine organic catalyst. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 552–561.
  - 3 Jitonnorn, J.; Meelua, W. Cationic ring-opening polymerization of cyclic carbonates and lactones by group 4 metallocenes: a theoretical study on mechanism and ring-strain effects. *J. Theor. Comput. Chem.* **2016**, *16*, 1750003.
  - 4 Lu, M.; Zhu, X.; Li, X.; Yang, X.; Tu, Y. Synthesis of cyclic oligo(ethylene adipate)s and their melt polymerization to poly(ethylene adipate). *Chinese J. Polym. Sci.* **2017**, *35*, 1051–1060.
  - 5 Song, Q.; Hu, S.; Zhao, J.; Zhang, G. Organocatalytic copolymerization of mixed type monomers. *Chinese J. Polym. Sci.* **2017**, *35*, 581–601.
  - 6 Pascual, A.; Sardon, H.; Veloso, A.; Ruipérez, F.; Mecerreyes, D. Organocatalyzed synthesis of aliphatic polyesters from ethylene brassylate: a cheap and renewable macrolactone. *ACS Macro Lett.* **2014**, *3*, 849–853.
  - 7 Pascual, A.; Sardón, H.; Ruipérez, F.; Gracia, R.; Sudam, P.; Veloso, A.; Mecerreyes, D. Experimental and computational studies of ring-opening polymerization of ethylene brassylate macrolactone and copolymerization with  $\epsilon$ -caprolactone and TBD-guanidine organic catalyst. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 552–561.
  - 8 Ofstead, E. A.; Calderon, N. Equilibrium ring-opening polymerization of mono- and multicyclic unsaturated monomers. *Makromol. Chem.* **1972**, *154*, 21–34.
  - 9 Duda, A.; Kowalski, A.; Libiszowski, J.; Penczek, S. Thermodynamic and kinetic polymerizability of cyclic esters. *Macromol. Symp.* **2005**, *224*, 71–84.
  - 10 Li, X.; Li, H.; Zhao, Y.; Tang, X.; Ma, S.; Gong, B.; Li, M. Facile synthesis of well-defined hydrophilic polyesters as degradable poly(ethylene glycol)-like biomaterials. *Polym. Chem.* **2015**, *6*, 6452–6456.
  - 11 Schneiderman, D. K.; Hillmyer, M. A. Aliphatic polyester block polymer design. *Macromolecules* **2016**, *49*, 2419–2428.
  - 12 Steele, R. in *Polyester: 50 years of achievement*, Brunnschweiler, D. and Hearle, J. S. (Eds), The Textile Institute, Manchester, UK, **1993**, pp. 48–51.
  - 13 Turner, S. R.; Voit, B. I.; Mourey, T. H. All-aromatic hyperbranched polyesters with phenol and acetate end groups: Synthesis and characterization. *Macromolecules* **1993**, *26*, 4617–4623.
  - 14 Brunelle, D. J.; Boden, E. P.; Shannon, T. G. Remarkably selective formation of macrocyclic aromatic carbonates: Versatile new intermediates for the synthesis of aromatic polycarbonates. *J. Am. Chem. Soc.* **1990**, *112*, 2399–2402.
  - 15 Brunelle, D. J.; Bradt, J. E.; Serth-Guzzo, J.; Takekoshi, T.; Evans, T. L.; Pearce, E. J.; Wilson, P. R. Semicrystalline polymers via ring-opening polymerization: preparation and polymerization of alkylene phthalate cyclic oligomers. *Macromolecules* **1998**, *31*, 4782–4790.
  - 16 Brunelle, D. J. Cyclic oligomer chemistry. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1151–1164.
  - 17 Monvisade, P.; Loungvanidprapa, P. Synthesis of poly(ethylene terephthalate-co-isophthalate) via ring-opening polymerization of their cyclic oligomers. *J. Polym. Res.* **2008**, *15*, 381–387.
  - 18 Conzatti, L.; Utzeri, R.; Hodge, P.; Stagnaro, P. A novel tin-based imidazolium-modified montmorillonite catalyst for the preparation of poly(butylene terephthalate)-based nanocomposites using *in situ* entropically-driven ring-opening polymerization. *RSC Adv.* **2015**, *5*, 6222–6231.
  - 19 Pepels, M. P. F.; van der Sanden, F.; Gubbels, E.; Duchateau, R. Catalytic ring-opening (co)polymerization of semiaromatic and aliphatic (macro)lactones. *Macromolecules* **2016**, *49*, 4441–4451.
  - 20 Carlos Morales-Huerta, J.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. Poly(alkylene 2,5-furandicarboxylate)s (PEF and PBF) by ring opening polymerization. *Polymer* **2016**, *87*, 148–158.
  - 21 Sousa, A. F.; Guigo, N.; Pozyska, M.; Delgado, M.; Soares, J.; Mendonca, P. V.; Coelho, J. F. J.; Sbirrazzuoli, N.; Silvestre, A. J. D. Tailored design of renewable copolymers based on poly(1,4-butylene 2,5-furandicarboxylate) and poly(ethylene glycol) with refined thermal properties. *Polym. Chem.* **2018**, *9*, 722–731.
  - 22 Morales-Huerta, J. C.; Ilarduya, A.; Muñoz-Guerra, S. Blocky poly( $\epsilon$ -caprolactone-co-butylene 2,5-furandicarboxylate) copolyesters via enzymatic ring opening polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 290–299.
  - 23 Wu, J.; Xie, H.; Wu, L.; Li, B.; Dubois, P. DBU-catalyzed biobased poly(ethylene 2,5-furandicarboxylate) polyester with rapid melt crystallization: Synthesis, crystallization kinetics and melting behavior. *RSC Adv.* **2016**, *6*, 101578–101586.
  - 24 Rabnawaz, M.; Wyman, I.; Auras, R.; Cheng, S. A roadmap towards green packaging: The current status and future outlook for polyesters in the packaging industry. *Green Chem.* **2017**, *19*, 4737–4753.
  - 25 Xu, Q.; Chen, J.; Huang, W.; Qu, T.; Li, X.; Li, Y.; Yang, X.; Tu, Y. One pot, one feeding step, two-stage polymerization synthesis and characterization of (PTT-*b*-PTMO-*b*-PTT)<sub>n</sub> multiblock copolymers. *Macromolecules* **2013**, *46*, 7274–7281.
  - 26 Chen, J.; Chen, D.; Huang, W.; Yang, X.; Li, X.; Tu, Y.; Zhu, X. A one pot facile synthesis of poly(butylene terephthalate)-block-poly(tetramethylene oxide) alternative multiblock copolymers via PROP method. *Polymer* **2016**, *107*, 29–36.
  - 27 Zhu, X.; Gu, J.; Li, X.; Yang, X.; Wang, L.; Li, Y.; Li, H.; Tu, Y. PROP: an *in situ* cascade polymerization method for the facile synthesis of polyesters. *Polym. Chem.* **2017**, *8*, 1953–1962.
  - 28 Zhang, M.; Gu, J.; Zhu, X.; Gao, L.; Li, X.; Yang, X.; Tu, Y.; Li, C. Y. Synthesis of poly(butylene terephthalate)-block-poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) multiblock terpolymers via a facile PROP method. *Polymer* **2017**, *130*, 199–208.
  - 29 Chen, J.; Huang, W.; Xu, Q.; Tu, Y.; Zhu, X.; Chen, E. PBT-*b*-PEO-*b*-PBT triblock copolymers: Synthesis, characterization and double-crystalline properties. *Polymer* **2013**, *54*, 6725–6731.
  - 30 Pepels, M. P.; van der Sanden, F.; Gubbels, E.; Duchateau, R. Catalytic ring-opening (co)polymerization of semiaromatic and aliphatic (macro)lactones. *Macromolecules* **2016**, *49*, 4441–4451.
  - 31 Duda, A.; Penczek, S. Thermodynamics, kinetics, and mechanisms of cyclic esters polymerization. In *Polymers from Renewable Resources*, American Chemical Society. **2001**, Vol. 764, pp 160–198.
  - 32 Nishida, H.; Yamashita, M.; Endo, T.; Tokiwa, Y. Equilibrium polymerization behavior of 1,4-dioxan-2-one in bulk. *Macromolecules* **2000**, *33*, 6982–6986.
  - 33 Hejl, A.; Scherman, O. A.; Grubbs, R. H. Ring-opening metathesis polymerization of functionalized low-strain monomers with ruthenium-based catalysts. *Macromolecules* **2005**, *38*, 7214–7218.
  - 34 Burch, R. R.; Lustig, S. R.; Spinu, M. Synthesis of cyclic oligoesters and their rapid polymerization to high molecular weight. *Macromolecules* **2000**, *33*, 5053–5064.
  - 35 Scheirs, J. and Long, T. E. in *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, John Wiley & Sons, **2005**.