Chinese Journal of
POLYMER SCIENCE

RESEARCH ARTICLE

https://doi.org/10.1007/s10118-024-3127-3
Chinese J. Polym. Sci.

Controllable Ring-opening Polymerization of δ-Valerolactone Catalyzed by Quinolinyl-Urea/MTBD Systems

Xin-Yu Liu, Liang Zhu, Su-Yun Jie*, and Bo-Geng Li

State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, China

Abstract Due to their excellent biocompatibility and biodegradability, aliphatic polyesters are widely used in the biomedical, packaging and agricultural fields, which are usually accessed by the ring-opening polymerization (ROP) of lactones and the catalysts particularly play an important role. Herein a series of quinolinyl-urea catalysts have been synthesized *via* the reaction between isocyanate and aminoquinoline with an amino group at different substitution positions and characterized. In combination with 7-methyl-1, 5, 7-triazabicyclo[4,4,0]dec-5-ene (MTBD) as a cocatalyst and benzyl alcohol (BnOH) as an initiator, 1-(3,5-bis(trifluoromethyl)phenyl)-3-(quinolin-3-yl)urea (**3-QU**) was observed to be most active for the ROP of δ-valerolactone (δ-VL). The polymerization conditions were optimized by varying the type of organic base, catalyst concentration and reaction temperature. By changing the ratio of $[M]_0/[I]$, linear polyvalerolactones (PVLs) with different molecular weights and narrow molecular weight distribution were prepared. The kinetic and chain extension experiments were carried out to prove the "living"/controllable feature. And the NMR experiments were used to support the proposal of possible mechanism.

Keywords Quinolinyl-urea; Ring-opening polymerization; PVL

Citation: Liu, X. Y.; Zhu, L.; Jie, S. Y.; Li, B. G. Controllable ring-opening polymerization of δ-valerolactone catalyzed by quinolinyl-urea/MTBD systems. *Chinese J. Polym. Sci*. https://doi.org/10.1007/s10118-024-3127-3

INTRODUCTION

Due to their flexibility, strength, versatility, durability and low cost, the global production of plastics is growing exponentially, and plastics are ubiquitous and indispensable in modern society.[1] The widespread use of plastics inevitably generates large amounts of plastic waste, yet these materials are resistant to degradation, persist for long periods of time in the environment and cause significant plastic pollution.[2,3] Aliphatic polyesters, including polyvalerolactone (PVL), polycaprolactone (PCL), poly(lactic acid) (PLA), *etc*., are an excellent class of biodegradable polymer materials that have shown particular relevance in the development of sustainable and degradable polymers to address the environmental issues.[4–6] They are usually derived from the renewable resources and can be recycled, composted and incinerated with a low environmental impact, are biocompatible, biodegradable and renewable and have a wide range of applications in the biomedical, packaging and agricultural fields.[7–13] Due to the presence of a large number of ester groups in the polymer main chains, aliphatic polyesters are easily hydrolyzed and degraded by various microorganisms or enzymes, and the degradation products are non-polluting and non-toxic.[14–17]

One of the most common synthetic routes for the synthesis of aliphatic polyesters is the transition metal catalyzed ring-opening polymerization (ROP) of lactones. However, in the biomedical, packaging and agricultural fields, the removal of metal contaminants bound to the chain ends must be considered,[18] which have driven research interest into metal-free organic catalyzed synthesis of aliphatic polyesters.[19–24] In this context, the pursuit of efficient and economical organic catalysts and precise control of ROP have become major challenges. Among the organic catalysts used for the ROP of lactones, the urea or thiourea catalysts were very efficient and controllable when they were combined with a base, such as MTBD or alkoxide.[25–32]

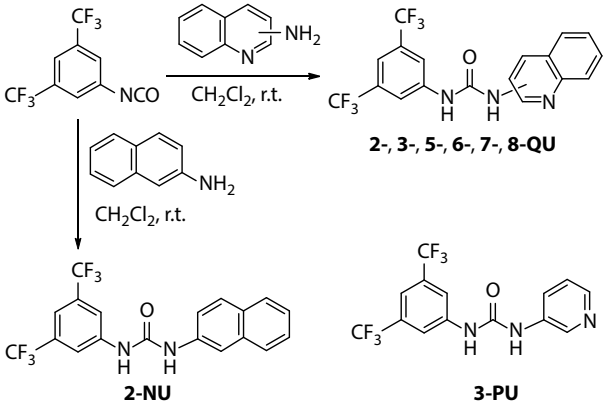
Although the diverse substituents (*i.e*., cyclohexyl, phenyl, phosphorene) on the nitrogen atom of urea group have been comprised in the urea catalysts, there were few reports about the incorporation of heterocycles into the urea structures except that we have developed several different types of heterocyclic urea catalysts and used them in the (co)ROP of δ-valerolactone (δ-VL), ε-caprolactone (ε-CL) and L-lactide (*L*-LA) with high activity and controllability.[33–37] In comparison with the symmetric phenyl ring, the heterocyclic substituents have a nonuniform distribution of electron density. Therefore, the catalytic activity would be affected when they were incorporated into the urea catalysts. We found that the pyridyl-urea catalysts with various substituents were very active and controllable in the ROP of δ-VL, ε-CL and trimethylene carbonate (TMC) in combination with MTBD.[33–35] Considering the similarities and differences between a phenyl ring and a pyridyl ring, it was interesting and meaningful for us to investigate

* Corresponding author, E-mail: jiesy@zju.edu.cn

Received January 25, 2024; Accepted March 20, 2024; Published online April 25, 2024

the synergistic effects of combining a phenyl ring and a pyridine ring on the catalytic performance. Therefore, the quinolinyl group with a urea group at different substitution positions just fitted our requirement and was introduced into the urea-based catalysts to develop a novel type of urea catalysts for the catalytic ROP of lactones.

Herein, a series of quinolinyl-urea catalysts with a urea group at different substituent positions of quinoline ring were synthesized and applied in the ROP of δ-VL in combination with MTBD under different conditions. Meanwhile, a naphthyl-urea and a pyridyl-urea catalysts (**2-NU** and **3-PU**, Scheme 1) were also used for comparison.



Scheme 1 Synthesis of quinolinyl- and naphthyl-urea catalysts and structure of **3-PU**.

EXPERIMENTAL

Materials

All the chemicals were purchased and used as received unless stated otherwise. 3-Aminopyridine (99%,), 2-naphthylamine (99%), 3-aminoquinoline (99%), 3,5-bis(trifluoromethyl) phenyl isocyanate (98%), and dimethyl sulfoxide-d_6 (99%) were purchased from J&K Scientific Ltd., China. Benzoic acid (99.5%, Aladdin, China), anhydrous methanol (≥99.5%, Sinopharm Chemical Reagent Co., Ltd., China), calcium hydride (CaH_2, 93%, J&K Scientific Ltd., China), and chloroform-d (Sinopharm Chemical Reagent Co., Ltd., China) were used as received. δ-Valerolactone (δ-VL, 98.5%, J&K Scientific Ltd., China) and benzyl alcohol (BnOH, ≥99%, Aladdin, China) were dried over CaH_2 for 24 h and then distilled under reduced pressure. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, 98%), 4-dimethylaminopyridine (DMAP, 99%), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%) (J&K Scientific Ltd., China) were dried over 4 Å molecular sieves. Tetrahydrofuran (THF, 98%, Sinopharm Chemical Reagent Co., Ltd., China), dichloromethane (DCM, 98%, Sinopharm Chemical Reagent Co., Ltd., China), toluene and *n*-hexane (99%, Aladdin, China) were purified through solvent purification systems (MB-SPS, MBRAUN). 3-Pyridyl-urea catalyst (**3-PU**) was prepared for comparison according to our previous procedure.[33]

Characterization

FTIR spectra were recorded on a Thermo-Fisher Nicolet iS50 Fourier Infrared Spectrometer in the range of 4000–400 cm^{-1} using KBr disks. All the proton and carbon nuclear magnetic resonance (^{1}H- and ^{13}C- NMR) spectra were recorded on a 400 MHz Bruker AVANCE II NMR spectrometer (Bruker BioSpin Co., Switzerland) at room temperature in $CDCl_3$ (for PVLs) or DMSO-d_6 (for catalysts) using TMS as the internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet. The monomer conversion was calculated by comparing the integral of characteristic signals from the remaining monomer with that of corresponding signals from the polymer. Molecular weight ($M_{n,NMR}$) of isolated polymers was determined by comparison of signal integrals from the end group with the repeat units. Elemental analysis was performed on a German Vario MAX cube elemental analyzer. Molecular weight ($M_{n,GPC}$) and molecular weight distribution ($Đ$) of the polymers were measured by GPC using a Waters 1515/2414 series system in THF (3 mg/mL) at 35 °C at a flow rate of 1 mL/min and calibrated with polystyrene standards. MALDI-TOF MS results were obtained using a Bruker Ultraflex TOF mass spectrometer equipped with a modified Nd: yttrium aluminum garnet laser (355 nm). The MS results were recorded in purified THF (2 mg/mL) at 25 °C in a linear mode using 2,5-dihydroxybenzoic acid as the matrix.

Synthesis of Quinolinyl- and Naphthyl-urea Catalysts

*1-(3,5-bis(trifluoromethyl)phenyl)-3-(quinolin-2-yl)urea (**2-QU**)*

To a dried 50 mL Schlenk flask, 2-aminoquinoline (288 mg, 2.0 mmol) and ultra-dry dichloromethane (5 mL) were added sequentially. After the material was completely dissolved, 3,5-bis(trifluoromethyl)phenyl isocyanate (0.35 mL, 2.0 mmol) was added dropwise to the flask with a syringe. The reaction mixture was stirred at room temperature for 1 h and the white precipitate was centrifuged and washed for 3 times with dichloromethane. The product was isolated as a white powder in a yield of 53.8%. FTIR (KBr disk, *v*, cm^{-1}): 3317, 1703, 1571, 1504, 1476, 1444, 1382, 1349, 1276, 1223, 1175, 1133, 1050, 955, 886, 857, 789, 745, 725, 700, 681. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 9.50 (s, 1H), 9.27 (s, 1H), 8.29 (d, *J*=2.2 Hz, 1H), 8.12 (s, 2H), 7.73 (m, 2H), 7.68 (m, 2H), 7.46 (m, 2H). ^{13}C-NMR (101 MHz, DMSO-d_6, δ, ppm): 166.7, 151.9, 147.9, 137.5, 136.5, 131.5, 129.0, 126.7, 125.4, 124.4, 122.2, 121.6, 118.7, 111.7. Anal. Calcd. For $C_{18}H_{11}F_6N_3O$ (399.29): C, 53.12; H, 2.51; N, 10.89. Found: C, 54.15; H, 2.78; N, 10.52.

*1-(3,5-bis(trifluoromethyl)phenyl)-3-(quinolin-3-yl)urea (**3-QU**)*

Using the method described for **2-QU**, **3-QU** was obtained from the reaction between 3-aminoquinoline and 3,5-bis(trifluoromethyl)phenyl isocyanate as a white powder in a yield of 81.6%. FTIR (KBr disk, *v*, cm^{-1}): 3328, 1696, 1577, 1493, 1473, 1444, 1384, 1349, 1276, 1229, 1177, 1131, 1050, 952, 886, 850, 780, 747, 725, 702, 682. ^{1}H-NMR (DMSO-d_6, δ, ppm): 9.63 (s, 1H), 9.47 (s, 1H), 8.87 (d, *J*=2.4 Hz, 1H), 8.58 (d, *J*=2.4 Hz, 1H), 8.19 (s, 2H), 7.94 (t, *J*=7.4 Hz, 2H), 7.60 (m, 3H). ^{13}C-NMR (DMSO-d_6, δ, ppm): 152.7, 144.6, 143.9, 141.6, 132.9, 131.2, 130. 9, 130.6, 128.5, 128.0, 127.5, 127.1, 126.6, 124.4, 122.2, 121.5, 118.3, 118.2, 114.7. Anal. Calcd. For $C_{18}H_{11}F_6N_3O$ (399.29): C, 51.72; H, 3.01; N, 10.71. Found: C, 54.15; H, 2.78; N, 10.52.

*1-(3,5-bis(trifluoromethyl)phenyl)-3-(quinolin-5-yl)urea (**5-QU**)*

Using the method described for **2-QU**, **5-QU** was obtained from

the reaction between 5-aminoquinoline and 3,5-bis(trifluoromethyl)phenyl isocyanate as a white powder in a yield of 79.3%. FTIR (KBr disk, *v*, cm^{-1}): 3323, 1695, 1577, 1499, 1473, 1442, 1384, 1349, 1279, 1229, 1177, 1135, 1059, 957, 886, 850, 784, 753, 721, 706, 680. ^{1}H-NMR (DMSO-d_6, *δ*, ppm): 9.24 (s, 1H), 8.72 (s, 1H), 8.49 (d, *J*=4.0 Hz, 1H), 8.04 (d, *J*=8.0 Hz, 1H), 7.72 (s, 2H), 7.48 (d, *J*=7.2 Hz, 1H), 7.38 (d, *J*=8.0 Hz, 1H), 7.30 (m, 1H), 7.22 (s, 1H), 7.16 (m, 1H). ^{13}C-NMR (DMSO-d_6, *δ*, ppm): 152.9, 149.6, 141.6, 138.7, 136.5, 131.5, 131.1, 130.2, 129.0, 124.4,121.6, 120.2, 118.7, 116.2, 116.0. Anal. Calcd. For $C_{18}H_{11}F_6N_3O$ (399.29): C, 53.04; H, 3.01; N, 10.84. Found: C, 54.15; H, 2.78; N, 10.52.

*1-(3,5-bis(trifluoromethyl)phenyl)-3-(quinolin-6-yl)urea (**6-QU**)*

Using the method described for **2-QU**, **6-QU** was obtained from the reaction between 6-aminoquinoline and 3,5-bis(trifluoromethyl)phenyl isocyanate as a white powder in a yield of 80.7%. FTIR (KBr disk, *v*, cm^{-1}): 3321, 1705, 1573, 1491, 1479, 1444, 1385, 1345, 1276, 1230, 1178, 1131, 1058, 953, 887, 851, 780, 753, 728, 707, 689. ^{1}H-NMR (DMSO-d_6, *δ*, ppm): 9.53 (s, 1H), 9.38 (s, 1H), 8.76 (dd, J_1=7.8 Hz, J_2=2.0 Hz, 1H), 8.29 (d, *J*=7.8 Hz, 1H), 8.24 (d, *J*=2.4 Hz, 1H), 8.19 (s, 2H), 7.97 (d, *J*=8.0 Hz, 1H), 7.73 (dd, J_1=8.0 Hz, J_2=2.4 Hz, 1H), 7.67 (s, 1H), 7.48 (m, 1H). ^{13}C-NMR (DMSO-d_6, *δ*, ppm): 154.2, 148.8, 144.1, 141.8, 137.9, 131.1, 128.3, 128.1, 123.7, 121.92, 119.5, 118.1, 115.5, 113.6. Anal. Calcd. For $C_{18}H_{11}F_6N_3O$ (399.29): C, 52.12; H, 2.87; N, 10.96. Found: C, 54.15; H, 2.78; N, 10.52.

*1-(3,5-bis(trifluoromethyl)phenyl)-3-(quinolin-7-yl)urea (**7-QU**)*

Using the method described for **2-QU**, **7-QU** was obtained from the reaction between 7-aminoquinoline and 3,5-bis(trifluoromethyl)phenyl isocyanate as a white powder in a yield of 82.0%. FTIR (KBr disk, *v*, cm^{-1}): 3327, 1694, 1578, 1493, 1473, 1444, 1384, 1349, 1276, 1229, 1177, 1131, 1050, 952, 886, 850, 780, 747, 725, 702, 682. ^{1}H-NMR (DMSO-d_6, *δ*, ppm): 9.56 (s, 1H), 9.44 (s, 1H), 8.83 (dd, J_1=4.2 Hz, J_2=1.8 Hz, 1H), 8.25 (m, 2H), 8.17 (s, 2H), 7.91 (d, *J*=8.8 Hz, 1H), 7.68 (m, 2H), 7.39 (m, 1H). ^{13}C-NMR (DMSO-d_6, *δ*, ppm): 152.9, 149.0, 146.6, 140.5, 136.5, 134.8, 131.5, 129.4, 129.0, 124.4, 123.8, 121.6, 118.7, 116.7, 110.7. Anal. Calcd. For $C_{18}H_{11}F_6N_3O$ (399.29): C, 50.98; H, 3.39; N, 10.49. Found: C, 54.15; H, 2.78; N, 10.52.

*1-(3,5-bis(trifluoromethyl)phenyl)-3-(quinolin-8-yl)urea (**8-QU**)*

Using the method described for **2-QU**, **8-QU** was obtained from the reaction between 8-aminoquinoline and 3,5-bis(trifluoromethyl)phenyl isocyanate as a white powder in a yield of 78.3%. FTIR (KBr disk, *v*, cm^{-1}): 3328, 1696, 1577, 1490, 1479, 1447, 1389, 1348, 1273, 1221, 1180, 1134, 1049, 953, 890, 854, 781, 750, 728, 705, 680. ^{1}H-NMR (DMSO-d_6, *δ*, ppm): 10.60 (s, 1H), 9.78 (s, 1H), 8.92 (d, *J*=4.4 Hz, 1H), 8.55 (dd, J_1=7.2 Hz, J_2=2.0 Hz, 1H), 8.39 (dd, J_1=7.2 Hz, J_2=2.0 Hz, 1H), 8.13 (s, 2H), 7.64 (m, 2H), 7.57 (m, 2H), 7.46 (t, *J*=2.4 Hz, 1H). ^{13}C-NMR (DMSO-d_6, *δ*, ppm): 148.6, 137.2, 136.7, 133.8, 131.5, 129.2, 129.0, 127.3, 124.4, 121.2, 118.7, 116.5, 113.8. Anal. Calcd. For $C_{18}H_{11}F_6N_3O$ (399.29): C, 53.05; H, 2.92; N, 11.01. Found: C, 54.15; H, 2.78; N, 10.52.

*1-(3,5-bis(trifluoromethyl)phenyl)-3-(naphthalen-2-yl)urea (**2-NU**)*

Using the method described for **2-QU**, **2-NU** was obtained from the reaction between 2-naphthylamine and 3,5-bis(trifluoromethyl)phenyl isocyanate as a pink powder in a yield of 64.9%. FTIR (KBr disk, *v*, cm^{-1}): 3277, 3100, 1654, 1558, 1388, 1284, 1128, 813, 740, 683. ^{1}H-NMR (DMSO-d_6, *δ*, ppm): 9.49 (s, 1H), 9.22 (s, 1H), 8.18 (m, 3H), 7.90 (m, 3H), 7.65 (s, 1H), 7.54 (dd, J_1=8.8 Hz, J_2=2.2 Hz, 1H), 7.47 (dd, J_1=8.3, J_2=6.8, 1H), 7.38 (d, *J*=2.4 Hz, 1H). ^{13}C-NMR (DMSO-d_6, *δ*, ppm): 152.5, 141.8, 136.6, 133.6, 130.7 (q, *J*=32.6 Hz, Ar-C-CF_3), 129.4, 128.4, 127.4, 127.1, 126.4, 124.2, 123.3, 119.9, 118.0, 118.0, 114.4. Anal. Calcd. For $C_{19}H_{12}F_6N_2O$ (398.31): C, 57.29; H, 3.04; N, 7.03. Found: C, 57.15; H, 2.78; N, 7.52.

General procedures for the ROP of *δ*-valerolactone

Bulk polymerization

A typical procedure for bulk polymerization is as follows (entry 2 in Table 1). In a dried 10 mL Schlenk flask with a stirring bar, the catalyst (**3-QU**, 21.96 mg, 0.055 mmol, 1 equiv.) was added and then purged for 3 times with high-purity hydrogen. MTBD (7.9 μL, 0.055 mmol, 1 equiv.), benzyl alcohol (5.7 μL, 0.055 mmol, 1 equiv.), and *δ*-VL (1 mL, 11.0 mmol, 200 equiv.) were then added sequentially. The reaction mixture was stirred at 25 °C for 10 min and then an appropriate amount of benzoic acid in dichloromethane was added to quench the reaction. A small amount was diluted in $CDCl_3$ to measure ^{1}H-NMR and calculate the conversion of monomer. The mixture was then poured into cold methanol and the precipitate was centrifuged. The obtained white solid was redissolved and reprecipitated and this process was repeated twice to purify the product, which was finally dried at 30 °C under vacuum to constant weight.

Solution polymerization

A typical procedure for solution polymerization in toluene is as follows. In a dried 10 mL Schlenk flask with a stirring bar, the catalyst (**3-QU**, 79.86 mg, 0.2 mmol) was first added and then purged for 3 times with high-purity nitrogen. benzyl alcohol (16.4 μL, 0.16 mmol), toluene (4 mL) and *δ*-VL (0.72 mL, 8.0

Table 1 ROP of *δ*-VL catalyzed by different quinolinyl-urea/MTBD system. [a]

Entry	Cat.	Time (min)	Conv. [b] (%)	$M_{n,th}$ [c] (kg/mol)	$M_{n,NMR}$ [b] (kg/mol)	$M_{n,GPC}$ [d] (kg/mol)	$Đ$ [d]
1	**2-QU**	300	30.6	6.2	4.3	–	–
2	**3-QU**	10	98.6	19.9	20.4	27.0	1.06
3	**5-QU**	30	98.9	19.9	26.5	29.5	1.08
4	**6-QU**	10	96.3	19.4	18.0	25.3	1.10
5	**7-QU**	40	74.8	15.1	16.6	–	–
6	**8-QU**	180	45.4	9.2	9.4	–	–
7	**2-NU**	10	96.3	19.4	19.7	28.5	1.14
8 [e]	**3-PU**	10	92.0	18.4	17.5	21.6	1.10

[a] Polymerization conditions: solvent-free, amount of *δ*-VL: 1 mL (11.0 mmol), catalyst loading: 0.5 mol% of monomer, [Cat]/[MTBD] = 1/1, $[M]_0/[I]$ = 200/1, reaction temperature: 25 °C, quenched with benzoic acid dissolved in dichloromethane; [b] Calculated by ^{1}H-NMR spectroscopy; [c] $M_{n,th} = [M]_0/[I] \times$ Conv.% × 100.12 + 108.14; [d] Measured by GPC in THF at 35 °C, calibrated with polystyrene standards; [e] Results in Ref. [33].

https://doi.org/10.1007/s10118-024-3127-3

mmol) were successively added. After all the materials dissolved completely, MTBD (28.8 μL, 0.2 mmol) was added to start the polymerization. The reaction solution was stirred at 25 °C for 45 min and quenched by the addition of excess benzoic acid dissolved in dichloromethane. A small amount was diluted in $CDCl_3$ to calculate the conversion of monomer by ^{1}H-NMR. The mixture was precipitated by pouring the mixture into cold anhydrous methanol and then filtered. The obtained solid was redissolved and reprecipitated and this process was repeated two times to purify the product, which was finally dried at 30 °C under vacuum to constant weight.

RESULTS AND DISCUSSION

Synthesis and Characterization of Quinolinyl- and 2-Naphthyl-urea Catalysts

All the quinolinyl- (**2-**, **3-**, **5-**, **6-**, **7-**, **8-QU**) and 2-naphthyl-urea (**2-NU**) catalysts were prepared *via* the reaction between 3,5-bis(trifluoromethyl)phenyl isocyanate and the corresponding aminoquinoline with an amino group at the 2-, 3-, 5-, 6-, 7-, 8-position or 2-naphthylamine in dichloromethane at room temperature (Scheme 1). All these catalysts were isolated as white or pink powders in good yield and characterized by FTIR, ^{1}H- and ^{13}C-NMR, and elemental analysis, with the results well consistent with their structures.

Ring-opening Polymerization of *δ*-VL

Bulk polymerization

All the above synthesized quinolinyl-urea catalysts were firstly used in the bulk ROP of *δ*-VL to evaluate their catalytic properties, in combination with MTBD as a cocatalyst and benzyl alcohol (BnOH) as a typical initiator (Table 1). Due to the different positions of urea group on the quinoline ring in their structures, **2-QU**, **3-QU**, **5-QU**, **6-QU**, **7-QU** and **8-QU** have different catalytic activities. The quinolinyl-N atom on the quinoline ring will cause the uneven distribution of electrons, which will further affect the acidity of the active hydrogen in the urea group linked to the quinoline ring. In addition, the different substitution positions would result in the different steric hindrance around the urea group to a certain extent. These could lead to the differences in the catalytic activities of quinolinyl-urea catalysts. The quinolinyl-N atoms in **2-QU** and **8-QU** are close to the urea group and may form an intramolecular hydrogen bonding, leading to their much lower activities than other quinolinyl-urea catalysts and the conversions of 30.6% (**2-QU**) in 5 h and 45.4% (**8-QU**) in 3 h were obtained, respectively. The **2-NU** produced much higher activity than **2-QU**, indicating that the quinolinyl-N atom had large influence in the catalytic performance. The **3-QU** or **6-QU**/MTBD systems were much more active and almost all the monomer completely converted into the polymers in 10 min. **3-QU** was a little more active than **3-PU** with a similar structure, and the polymer produced by **3-QU**/MTBD system had very close molecular weight to the theoretical value with narrow molecular weight distribution (*Đ*=1.06). In short, the order of catalytic activities is as follows: **3-QU > 6-QU ≈ 2-NU > 5-QU > 7-QU> 8-QU > 2-QU**.

In order to investigate the influence of reaction conditions, including type of base, molar ratios of catalyst/base and monomer/initiator and reaction temperature, **3-QU** was used in the following ROP of *δ*-VL, as shown in Table 2. Among the organic bases used, MTBD was found to give the best results and an almost complete conversion was observed in 10 min producing PVLs with a narrow *Đ*. TBD has been reported to be an efficient catalyst for the ROP of lactones, in which the dual activation of monomer and initiator happened by TBD due to the existence of hydrogen atom.[38,39] However, when TBD was combined with a quinolinyl-urea catalyst, the complicated hydrogen bonding interactions between them might play a certain toxic role to the active centers whether for TBD or urea anion, further leading to a decrease in catalytic activity (entry 1 in Table 2). Therefore, MTBD was usually combined with urea catalysts as a cocatalyst. And the addition of DMAP

Table 2 ROP of *δ*-VL catalyzed by **3-QU**/base under different conditions. [a]

Entry	Base	Cat./MTBD	[Cat]/[M]$_0$	[M]$_0$/[I]	Temp. (°C)	Time (min)	Conv. [b] (%)	$M_{n,th}$ [c] (kg/mol)	$M_{n,NMR}$ [b] (kg/mol)	$M_{n,GPC}$ [d] (kg/mol)	$Đ$ [d]
1	TBD	1/1	0.5%	200	25	10	45.4	92	9.1	22.7	1.24
2	DBU	1/1	0.5%	200	25	10	27.0	5.5	4.6	–	–
3	DMAP	1/1	0.5%	200	25	10	<1	–	–	–	–
4	MTBD	0/1	0.5%	200	25	180	<1	–	–	–	–
5	MTBD	1/0	0.5%	200	25	180	<1	–	–	–	–
6	MTBD	1/0.5	0.5%	200	25	10	56.9	11.5	11.9	–	–
7	MTBD	1/1	0.5%	200	25	10	98.6	19.9	20.4	27.0	1.06
8	MTBD	1/2	0.5%	200	25	8	98.0	19.7	20.8	24.4	1.08
9	MTBD	1/1	0.25%	200	25	300	34.2	6.7	4.8	–	–
10	MTBD	1/1	0.5%	200	0	10	59.8	12.1	4.7	15.3	1.75
11	MTBD	1/1	0.5%	200	40	10	97.0	19.5	19.8	28.7	1.06
12	MTBD	1/1	0.5%	200	60	10	97.1	19.6	19.3	24.2	1.07
13	MTBD	1/1	0.5%	200	90	10	88.4	17.8	12.8	24.0	1.14
14	MTBD	1/1	0.5%	20	25	10	97.4	2.1	2.2	4.4	1.07
15	MTBD	1/1	0.5%	50	25	10	97.6	5.0	5.3	8.0	1.07
16	MTBD	1/1	0.5%	100	25	10	99.0	10.0	10.6	15.1	1.07
17	MTBD	1/1	0.5%	400	25	10	97.0	39.0	30.1	34.3	1.07
18 [e]	MTBD	1/1	0.5%	50+150	60	30	94.9	19.1	20.5	31.8	1.16

[a] Polymerization conditions: solvent-free, amount of *δ*–VL: 1 mL (11.0 mmol), catalyst: **3-QU**, [Cat]/[MTBD]=1/1, quenched with benzoic acid dissolved in dichloromethane. [b] Calculated by ^{1}H-NMR spectroscopy. [c] $M_{n,th}$ = [M]$_0$/[I] × Conv.% × 100.12 + 108.14; [d] Measured by GPC in THF at 35 °C, calibrated with polystyrene standards; [e] Chain extension experiment using PVL prepared as an initiator (entry 15).

https://doi.org/10.1007/s10118-024-3127-3

to the ROP reaction almost had no acceleration.

The amount of base used in the ROP reaction was also an important factor to influence the catalytic properties (entries 4–8 in Table 2). The **3-QU** catalyst or MTBD alone was almost inactive in the ROP of *δ*-VL even if the polymerization was performed for a longer time (3 h). When 0.5 equiv. of MTBD/**3-QU** was used, a monomer conversion of 56.9% was achieved in 10 min, although it was much lower than that with a 1/1 ratio of **3-QU**/MTBD (98.6%). The polymerization reaction was accelerated when the amount of MTBD increased to 1/2 and the monomer conversion reached 98% in 8 min with controllable molecular weight and molecular weight distribution of PVLs. However, fixing the molar ratio of **3-QU**/MTBD at 1/1, when the amount of catalyst was reduced to 0.25 mol%, the conversion was much lower (34.2% in 5 h, entry 9 in Table 2). Therefore, a catalyst amount of 0.5 mol% was chosen for the following studies.

The catalytic system **3-QU**/MTBD was very efficient in the ROP of *δ*-VL in the temperature range of 25–60 °C and almost complete monomer conversions (>97%) with very narrow molecular weight distributions of PVLs were obtained in 10 min. When the reaction temperature was increased to 90 °C, a slightly lower monomer conversion of 88.4% was obtained in 10 min (entry 13 in Table 2). The lower reaction temperature was relatively unfavourable to the ROP of *δ*-VL and a monomer conversion of 59.8% was achieved at 0 °C (entry 10 in Table 2). PVLs with different molecular weights were prepared by varying the molar ratio of monomer/initiator (entries 14–17 in Table 2). In the range of $[M]_0/[I]$ ratio from 20 to 200, not only high monomer conversions approaching 100% were observed, but also the molecular weights of PVLs fitted the theoretical values well and the molecular weight distributions were around 1.07 with the unimodal GPC curves (Fig. 1). When 400 of $[M]_0/[I]$ was used, the measured molecular weight of PVLs was lower than the theoretical value. This deviation was probably caused by the addition error of benzyl alcohol.

Solution polymerization

The catalytic properties of the **3-QU**/MTBD system in the solution polymerization of *δ*-VL were also evaluated in toluene and THF at 25 °C (Table 3). With a lower amount of catalyst (0.5 mol%), the ring-opening polymerization rate in solution was much lower than that in bulk polymerization. Therefore, the catalyst amount was increased to 2.5 mol% of monomer, the monomer conversions of 94.6% and 81.4% in 45 min were obtained with 50 equiv. of monomer in toluene and THF, respectively, and the polymers produced also had a narrow molecular weight distribution.

Living character of ROP

The living/controllable character of ROP of *δ*-VL catalyzed by **3-QU**/MTBD system could be confirmed by chain extension and

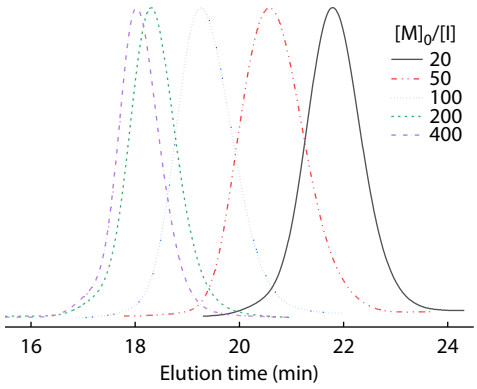


Fig. 1 GPC traces of PVLs with different molecular weights.

kinetic experiments. The chain extension experiment was carried out with a low-molecular-weight PVL as an initiator (M_n=5.3 kg/mol, $Đ$=1.07, entry 15 in Table 2) at 60 °C in order to make the PVL initiator completely dissolve in monomer. The second batch of 150 equiv. of *δ*-VL was then added and the 94.9% of monomer converted into polymers in 30 min. The chain extension of PVLs with a molecular weight of 20.5 kg/mol was obtained and the molecular weight distribution still remained narrow ($Đ$=1.16) as shown in Fig. 2. These results matched well with PVLs produced by the one-batch polymerization (entry 7 in Table 2), indicating that the ROP of *δ*-VL catalyzed by **3-QU**/MTBD system had "living"/controllable characteristics.

In order to further verify the controllability of **3-QU**/MTBD system in the ROP of *δ*-VL, the kinetic experiments were also performed in solution polymerization with a $[M]_0/[I]$ molar ratio of 50 at 25 °C in toluene (Fig. 3). A small amount (0.2 mL) was withdrawn from the reaction solution at an appropriate time interval by using a syringe and quickly quenched with a dichloromethane solution of benzoic acid and further characterized by ^{1}H-NMR and GPC. The linear relationship between $Ln([VL]_0/[VL])$ and reaction time was founded, indicating the first-order kinetics characteristic between the polymerization rate and monomer concentration. In addition, the molecular weight of PVLs from the aliquots linearly increased along with the increase of monomer conversion and all the molecular weight distribution maintained below 1.10, further confirming that the ROP of *δ*-VL catalyzed by **3-QU**/MTBD system was well controllable and had living character.

Possible mechanism for the ROP of δ-VL

In order to verify the catalytic mechanism for the ROP of *δ*-VL catalyzed by the **3-QU**/MTBD system, the ^{1}H- and ^{13}C- NMR spectra of pure **3-QU**, pure MTBD, and the mixture of **3-QU**/MTBD with 1/1 molar ratio were tested, as shown in Fig. 4. The solutions of pure **3-QU** and pure MTBD are colourless in DMSO, the colour change from colourless to yellow was observed when one equiv. of MTBD was added to the solution of **3-QU**, indicating that the interaction occurred between them. In

Table 3 Solution ROP of *δ*-VL catalyzed by **3-QU**/MTBD. [a]

Entry	Solvent	Conv. [b] (%)	$M_{n,th}$ [c] (kg/mol)	$M_{n,NMR}$ [b] (kg/mol)	$M_{n,GPC}$ [b] (kg/mol)	$Đ$
1	Toluene	94.6	4.8	4.4	6.7	1.07
2	THF	81.4	4.2	4.1	6.2	1.08

[a] Polymerization conditions: *δ*-VL: 0.72 mL (8.0 mmol), $[M]_0$=2 mol/L, catalyst loading: 2.5 mol% of monomer, [**3-QU**]/[MTBD]=1/1, initiator: BnOH, $[M]_0/[I]$=50/1, reaction time: 45 min, reaction temperature: 25 °C, quenched with benzoic acid dissolved in dichloromethane; [b] Calculated by ^{1}H-NMR spectroscopy; [c] $M_{n,th} = [M]_0/[I] \times Conv.\% \times 100.12 + 108.14$.

https://doi.org/10.1007/s10118-024-3127-3

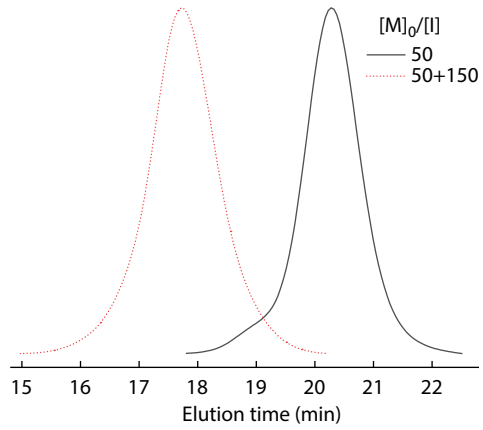


Fig. 2 GPC traces of low-molecular-weight PVLs and the PVLs after the chain expansion experiment (entries 15 and 18 in Table 2).

the ^{1}H-NMR spectra, after the addition of MTBD, two original peaks (9.63 and 9.47 ppm) for the NH signals of urea group in **3-QU** disappeared and a broad peak at 4.5–5.5 ppm appeared accordingly. In addition, the chemical shifts of other protons in **3-QU** and MTBD also changed more or less. In the ^{13}C-NMR spectra, the addition of MTBD led to the shift of many signals from a high field (pure **3-QU**) to a low field, such as those of the carbonyl-*C* atom (peak a) of urea group, the phenyl-C (peak e) and qunolinyl-C (peak d) atoms connected to urea group, *etc*. This was probably ascribed to the deprotonation of urea group and the electron delocalization. These chemical shifts also indicated the strong interaction between **3-QU** and MTBD.

Based on these above observation and no catalytic efficiency of pure **3-QU** or MTBD alone, a possible mechanism for the ROP of *δ*-VL catalyzed by the **3-QU**/MTBD system could be proposed in Scheme 2. Firstly, MTBD as a base captured one proton from the urea group in **3-QU** and the corresponding H^+ adduct of MTBD formed. Then, the deprotonated quinolinyl urea anion as an intermediate simultaneously activated initiator and monomer *via* the intermolecular hydrogen bonding interaction. The oxygen atom of activated benzyl alcohol attacked the carbonyl-C atom of *δ*-VL to make the ring opening and further resulted in the chain growth.

Characterization of PVLs

In the ^{1}H-NMR spectrum of synthesized PVLs in Fig. 5(a), the multiple peaks around 1.67 ppm, the triplet peaks at 2.34 and

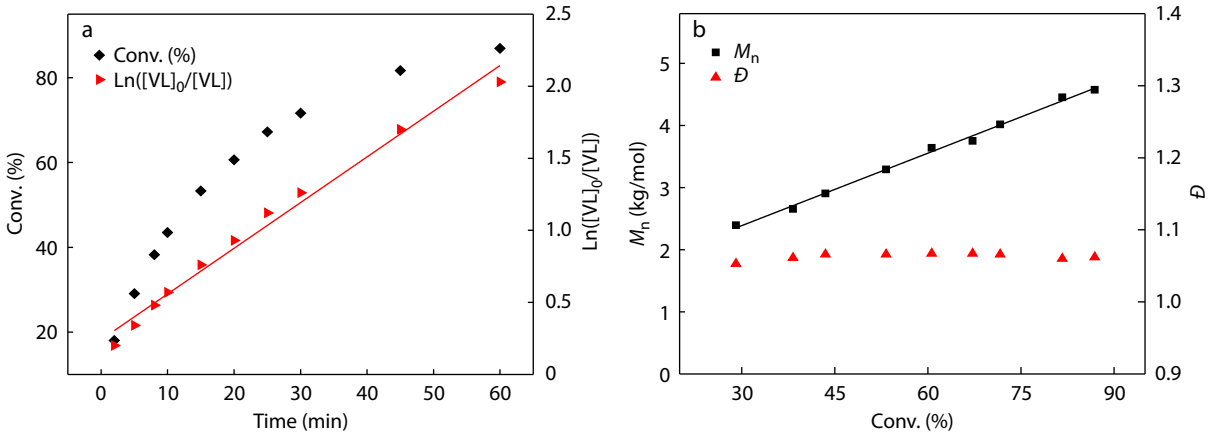


Fig. 3 Kinetic plots of Conv.(%) and Ln([VL]$_0$/[VL]) versus reaction time (a) and M_n and *Đ* of PVLs versus Conv.(%) (b) for the **3-QU**/MTBD-catalyzed ROP of *δ*-VL. Polymerization conditions: amount of *δ*-VL: 0.72 mL (8 mmol), [M]$_0$=2 mol/L in toluene, **3-QU**: 2.5 mol% of *δ*-VL, [**3-QU**]/[MTBD]=1/1, [M]$_0$/[I]=50, reaction temperature: 25 °C.

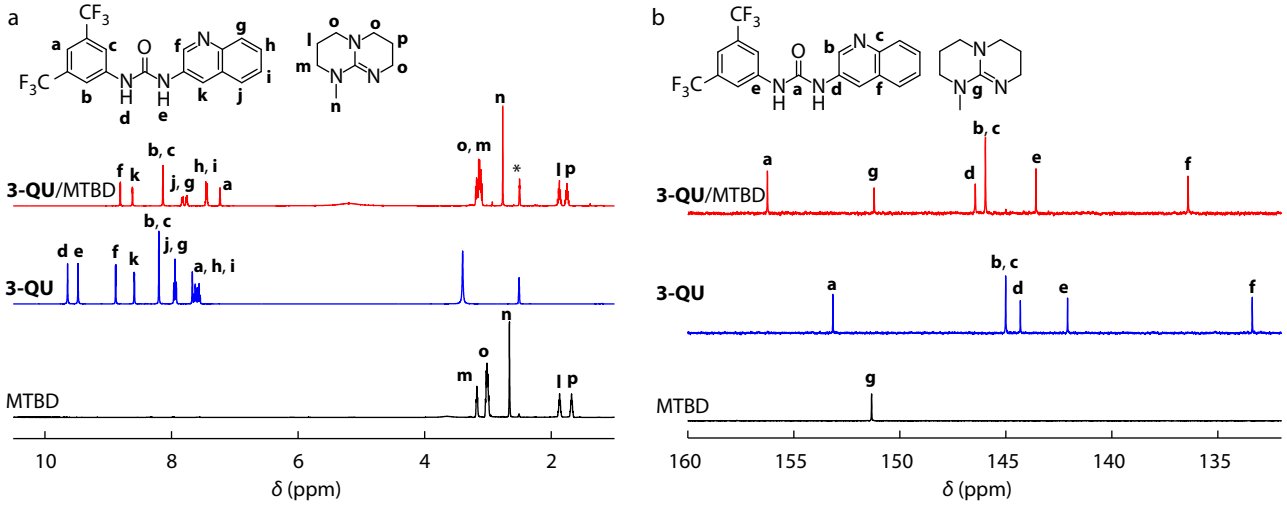
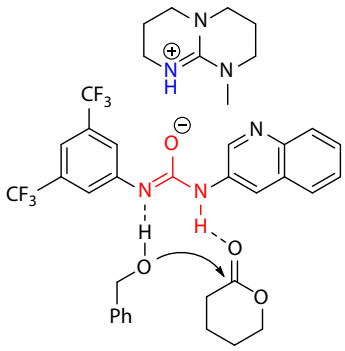


Fig. 4 (a) ^{1}H- and (b) ^{13}C-NMR spectra of the mixture of **3-QU**/MTBD with 1/1 molar ratio, pure **3-QU** and pure MTBD. * DMSO-d$_6$.

https://doi.org/10.1007/s10118-024-3127-3



Scheme 2 Proposed mechanism for the ROP of δ-VL catalyzed by **3-QU**/MTBD.

4.08 ppm were corresponded to the different methylene protons in the main chains of PVLs, respectively. The peaks at 7.36 and 5.12 ppm were assigned to the protons of phenyl ring and methylene group in the terminal benzyl group derived from the initiator. The characteristic signals of the methylene protons connected to hydroxyl group in the chain end located at 3.64 ppm as a triplet peak. All the above evidences indicated that the of δ-VL was successfully initiated by BnOH and the linear PVLs formed. This could be also proved by the ^{13}C-NMR spectrum (Fig. 5b), in which the signals of carbon atoms in the terminal benzyl group appeared at 128.2 and 66.2 ppm. The signal of methylene-C atom connected to hydroxyl group in the other chain end located at 62.2 ppm. The peaks at 173.2 ppm and 63.9, 33.7, 28.0, 21.4 ppm corresponded to the carbonyl-C and four consecutive methylene-C atoms in the repeat units.

In order to further confirm the structure of the PVLs, one sample (entry 15 in Table 2) was analysed by MALDI-TOF mass

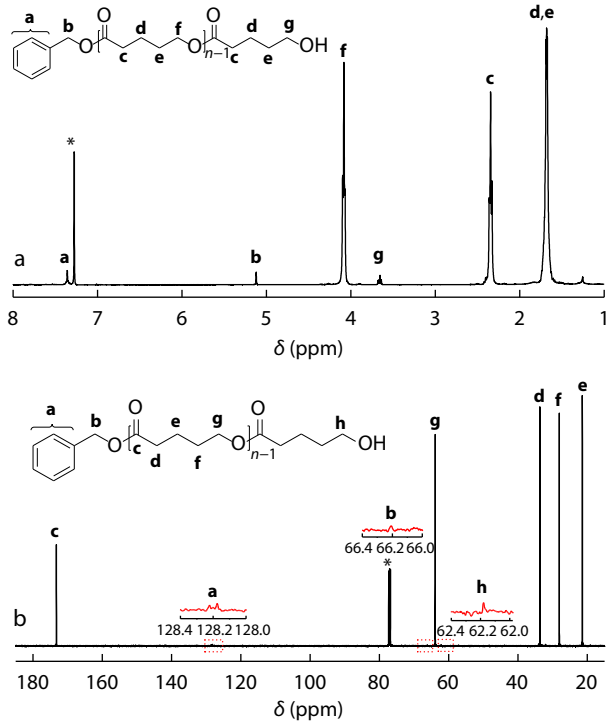


Fig. 5 (a) ^{1}H- and (b) ^{13}C- NMR spectra of synthesized PVLs. * $CDCl_3$.

spectroscopy as shown in Fig. 6. There were two main series of peaks perfectly consistent with the theoretical molecular weight of linear PVLs [BnO(VL)$_n$H] clustered with Na^+ and K^+ ions. For each series, the adjacent signals with the difference of 100 were separated by a VL repeating unit. Thus, the results of MALDI-TOF mass analysis were also in accordance with those of NMR analysis.

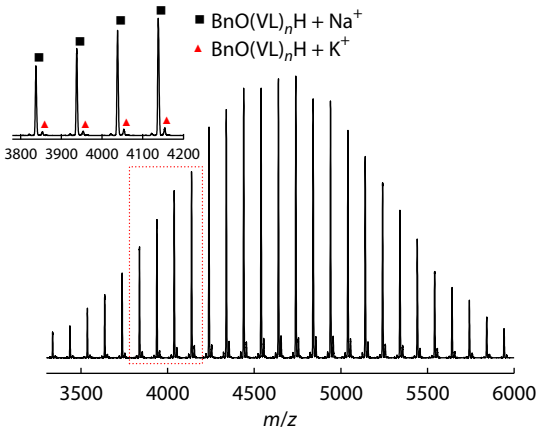


Fig. 6 MALDI-TOF MS of synthesized PVLs (entry 15 in Table 2).

CONCLUSIONS

In summary, a series of quinolinyl-urea catalysts with different substitution positions has been synthesized and investigated in the ring-opening polymerization of δ-VL in combination with MTBD. The different substitution positions had large influence on the catalytic properties and **3-QU** was found to be the most active. The **3-QU**/MTBD catalytic system required only 0.5 mol% catalyst concentration to initiate the ROP of δ-VL rapidly and kept highly active in the broad temperature range of 25–60 °C. Linear PVLs with different molecular weights and narrow molecular weight distribution were prepared by varying $[M]_0/[I]$ and the structures of PVLs were confirmed by NMR and MALDI-TOF mass spectroscopies. The "living"/controllable characteristic of ROP was verified by the kinetic experiments and chain extension reaction. Based on the NMR studies, a possible mechanism for the ROP of δ-VL was proposed.

Conflict of Interests

The authors declare no interest conflict.

ACKNOWLEDGMENTS

This work was financially supported by the National Key R&D Program of China (No. 2016YFC1100801).

REFERENCES

1 Geyer R.; Jambeck J. R.; Law K. L. Production, use, and fate of all plastics ever made. *Science* **2017**, *3*, e1700782.
2 Webb H. K.; Arnott J.; Crawford R. J.; Ivanova, E. P. Plastic degradation and its environmental implications with special reference to poly(ethylene terephthalate). *Polymers* **2012**, *5*,

1–18.
3 Duis K.; Coors A. Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects. *Environ. Sci. Eur.* **2016**, *28*, 2.
4 Schneiderman D. K.; Hillmyer M. A. Aliphatic polyester block polymer design. *Macromolecules* **2016**, *49*, 2419–2428.
5 Larranaga A.; Lizundia E. A review on the thermomechanical properties and biodegradation behaviour of polyesters. *Eur. Polym. J.* **2019**, *121*, 109296.
6 Brannigan R. P.; Dove A. P. Synthesis, properties and biomedical applications of hydrolytically degradable materials based on aliphatic polyesters and polycarbonates. *Biomater. Sci.* **2017**, *5*, 9–21.
7 Hillmyer M. A.; Tolman W. B. Aliphatic polyester block: renewable, degradable, and sustainable. *Acc. Chem. Res.* **2014**, *47*, 2390–2396.
8 Chiulan I.; Frone A.; Brandabur C.; Panaitescu D. M. Recent advances in 3D printing of aliphatic polyesters. *Bioengineering* **2018**, *5*, 2.
9 Arrieta M.; Samper M.; Aldas M.; López J. On the use of PLA-PHB blends for sustainable food packaging applications. *Materials* **2017**, *10*, 1008.
10 Pascouau C.; Wirotius A. L.; Carlotti S. Functional polyesters *via* ring-opening copolymerization of *α*-hydroxy-*γ*-butyrolactone and *ε*-caprolactone: La[N(SiMe$_3$)$_2$]$_3$ as an efficient coordination-insertion catalyst. *Eur. Polym. J.* **2023**, *185*, 111793.
11 Kim S. H.; Kim S. H.; Jung Y. TGF-β_3 encapsulated PLCL scaffold by a supercritical CO_2-HFIP co-solvent system for cartilage tissue engineering. *J. Control. Release* **2015**, *206*, 101–107.
12 Haas S.; Hain N.; Raoufi M.; Handschuh-Wang, S.; Wang, T.; Jiang, X.; Schönherr, H. Enzyme degradable polymersomes from hyaluronic acid-*block*-poly(ε-caprolactone) copolymers for the detection of enzymes of pathogenic bacteria. *Biomacromolecules* **2015**, *16*, 832–841.
13 Cha K. J.; Lih E.; Choi J.; Joung, Y. K.; Ahn, D. J.; Han, D. K. Shape-memory effect by specific biodegradable polymer blending for biomedical applications. *Macromol. Biosci.* **2014**, *14*, 667–678.
14 Sinha V. R.; Bansal K.; Kaushik R.; Kumria, R.; Trehan, A. Poly-*ε*-caprolactone microspheres and nanospheres: an overview. *Int. J. Pharm.* **2004**, *278*, 1–23.
15 Lam, C. X.; Teoh, S. H.; Hutmacher, D. W. Comparison of the degradation of polycaprolactone and polycaprolactone-(*β*-tricalcium phosphate) scaffolds in alkaline medium. *Polym. Int.* **2007**, *56*, 718–728.
16 Joshi, P.; Madras, G. Degradation of polycaprolactone in supercritical fluids. *Polym. Degrad. Stabil.* **2008**, *93*, 1901–1908.
17 Pena, J.; Corrales, T.; Izquierdo-Barba, I.; Doadrio, A.; Vallet-Regi, M. Long term degradation of poly(*ε*-caprolactone) films in biologically related fluids. *Polym. Degrad. Stabil.* **2006**, *91*, 1424–1432.
18 Dana, H. R.; Ebrahimi, F. Synthesis, properties, and applications of polylactic acid-based polymers. *Polym. Eng. Sci.* **2023**, *63*, 22–43.
19 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*, 5813–5840.
20 Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. Organocatalysis: opportunities and challenges for polymer synthesis. *Macromolecules* **2010**, *43*, 2093–2107.
21 Nzahou 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.
22 Hu, S.; Zhao, J.; Zhang, G.; Schlaad, H. Macromolecular architectures through organocatalysis. *Prog. Polym. Sci.* **2017**, *74*, 34–77.
23 Bossion, A.; Heifferon, K. V.; Meabe, L.; Zivic, N.; Taton, D.; Hedrick, J. L.; Long, T. E.; Sardon, H. Opportunities for organocatalysis in polymer synthesis *via* step-growth methods. *Prog. Polym. Sci.* **2019**, *90*, 164–210.
24 Xu, J.; Wang, X.; Liu, J.; Feng, X.; Gnanou, Y.; Hadjichristidis, N. Ionic H-bonding organocatalysts for the ring-opening polymerization of cyclic esters and cyclic carbonates. *Prog. Polym. Sci.* **2022**, *125*, 101484.
25 Zhang, X.; Jones, G. O.; Hedrick, J. L.; Waymouth, R. M. Fast and selective ring-opening polymerizations by alkoxides and thioureas. *Nature Chem.* **2016**, *8*, 1047–1053.
26 Fastnacht, K. V.; Spink, S. S.; Dharmaratne, N. U.; Pothupitiya, J. U.; Datta, P. P.; Kiesewetter E. T.; Kiesewetter, M. K. Bis- and tris-urea H-bond donors for ring-opening polymerization: unprecedented activity and control from an organocatalyst. *ACS Macro. Lett.* **2016**, *5*, 982–986.
27 Dharmaratne, N. U.; Pothupitiya,J. U.; Bannin, T. J.; Kazakov, O. I.; Kiesewetter, M. K. Triclocarban: commercial antibacterial and highly effective H-bond donating catalyst for ring-opening polymerization. *ACS Macro Lett.* **2017**, *6*, 421–425.
28 Lin B.; Waymouth, R. M. Urea anions: simple, fast, and selective catalysts for ring-opening polymerizations. *J. Am. Chem. Soc.* **2017**, *139*, 1645–1652.
29 Jain, I.; Malik, Payal. Advances in urea and thiourea catalyzed ring opening polymerization: a brief overview. *Eur. Polym. J.* **2020**, *133*, 109791.
30 Hewawasam, R. S.; Kalana,U. L. D. I.; Dharmaratne, N. U.; Wright, T. J.; Bannin, T. J.; Kiesewetter E. T.; Kiesewetter, M. K. *Macromolecules* **2019**, *52*, 9232–9237.
31 Du, F.; Zheng, Y.; Yuan, W.; Shan, G.; Bao, Y.; Jie S.; Pan, P. Solvent-free ring-opening polymerization of lactones with hydrogen-bonding bisurea catalyst. *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *57*, 90–100.
32 Zaky, M. S.; Guichard, G.; Taton, D. Structural effect of organic catalytic pairs based on chiral amino(thio)ureas and phosphazene bases for the isoselective ring-opening polymerization of racemic lactide. *Macromolecules* **2023**, *56*, 3607–3616.
33 Feng, R.; Jie, S.; Braunstein P.; Li, B. G. Pyridyl-urea catalysts for the solvent-free ring-opening polymerization of lactones and trimethylene carbonate. *Eur. Polym. J.* **2019**, *121*, 109293.
34 Feng, R.; Jie, S.; Braunstein P.; Li, B.-G. High molecular-weight cyclic polyesters from solvent-free ring-opening polymerization of lactones with a pyridyl-urea/MTBD. *Macromol. Chem. Phys.* **2020**, *221*, 2000075.
35 Feng, R.; Jie, S.; Braunstein P.; Li, B. G. Gradient copolymers of *ε*-caprolactone and *δ*-valerolactone *via* solvent-free ring-opening copolymerization with a pyridyl-urea/MTBD system. *J. Polym. Sci.* **2020**, *58*, 2108–2115.
36 Ji, C.; Jie, S.; Braunstein P.; Li, B. G. Fast and controlled ring-opening polymerization of *δ*-valerolactone catalyzed by benzoheterocyclic urea/MTBD catalysts. *Catal. Sci. Technol.* **2020**, *10*, 7555–7565
37 Ji, C.; Jie, S.; Li, B. G. Ring-opening copolymerization of L-lactide and *δ*-valerolactone catalyzed by benzoxazolyl urea catalyst/MTBD. *Acta Polymerica Sinica* (in Chinese) **2022**, *53*, 488–496.
38 Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Waymouth, R. M.; Hedrick, J. L. Triazabicyclodecene: A simple bifunctional organocatalyst for acyl transfer and ring-opening polymerization of cyclic esters. *J. Am. Chem. Soc.* **2006**, *128*, 4556–4557.
39 Simón L.; Goodman, J. M. The mechanism of TBD-catalyzed ring-opening polymerization of cyclic esters. *J. Org. Chem.* **2007**, *72*, 9656–9662.

https://doi.org/10.1007/s10118-024-3127-3