

N-Heterocyclic Olefins and Thioureas as an Efficient Cooperative Catalyst for Ring- Opening Polymerization of δ -Valerolactone

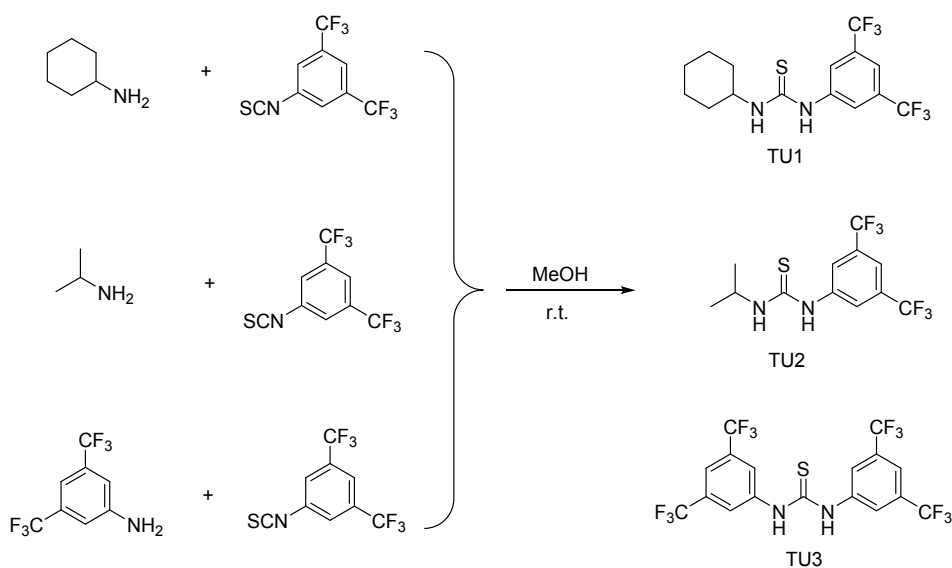
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1. General Experimental Procedure

Preparation of Thioureas

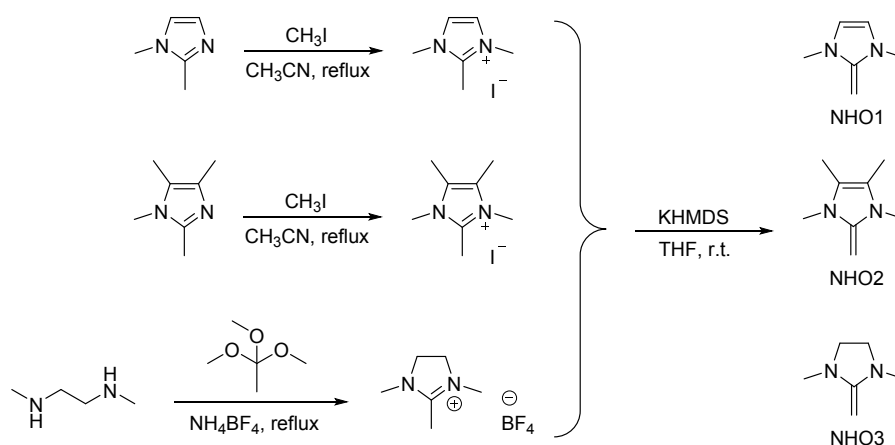
Thioureas are prepared by mixing the appropriate amine and isothiocyanate in a solution of MeOH (Scheme S1). The solution was stirred in the room temperature for 30 minutes. Then MeOH is removed under vacuum and the products were purified by washing with hexanes or pentane three times. After vacuum filtration, the filter residue was vacuum drying at 50 °C for 24 h. The spectra of thioureas (TU1, TU2, TU3) match those from the literature. [1]



Scheme S1. Schematic synthesis of TUs (TU1, TU2, TU3).

Preparation of NHOs

NHOs (NHO1, NHO2, NHO3) were prepared as described previously. [2] NHOs (NHO1, NHO2, NHO3) was synthesized by deprotonation of the corresponding precursor salt (Scheme S2) using KHMDS. The identity of target compounds NHO1, NHO2, NHO3 was confirmed by ^1H and ^{13}C NMR spectroscopy and they were stored in a glove box at -35 °C. For full characterization of NHO1, [3] NHO2, [4] NHO3, [5] see the cited literature.

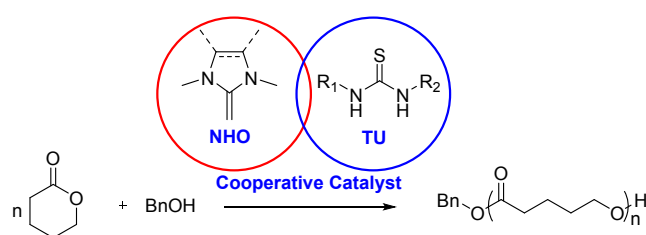


Scheme S2. Schematic synthesis of NHOs (NHO1, NHO2, NHO3).

References

- [1] Štrukil, V.; Igrc, M. D.; Eckert-Maksić, M.; Friščić, T. *Chem. Eur. J.*, **2012**, *18*, 8464-8473.
 [2] Chen, W. -C.; Shen, J. -S.; Jurca, T.; Peng, C. -J.; Lin, Y. -H.; Wang, Y. -P.; Shih, W. -C.; Yap, G. P. A.; Ong, T. -G. *Angew. Chem. Int. Ed.* **2015**, *127*, 15422 -15427.
 [3] Vitthal, B. S.; Bhalchandra M. B. *ChemSusChem*, **2016**, *9*, 1980-1985.
 [4] Kuhn, N.; Bohnen, H.; Kreutzberg, J.; Bläser, D.; Böse, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1136-1137.
 [5] Gruseck, U.; Heuschmann, M. *Chem. Ber.* **1987**, *120*, 2053-2064.

Typical procedure for polymerization of δ -VL



In an Ar-filled glovebox, the catalysts of NHO (0.05 mmol, 0.01 eq.), TU (0.1 mmol, 0.02 eq.) and initiator of BnOH (0.1 mmol, 0.02 eq.) were dissolved into 1 mL toluene in Schlenk tube. Then 0.45 mL δ -VL (5 mmol) was added via a syringe to the mixture solution. The reaction mixtures were stirred at room temperature. After the polymerization was completed, cool MeOH was added. The product was isolated by precipitation in *n*-hexane followed by drying thoroughly in vacuum.

Typical procedure for polymerization of δ -VL without BnOH

In an Ar-filled glovebox, the catalysts of NHO (0.05 mmol, 0.01 eq.), TU (0.1 mmol, 0.02 eq.) and were dissolved into 1 mL toluene in Schlenk tube. Then 0.45 mL δ -VL (5 mmol) was added via a syringe to the mixture solution. The reaction mixtures were stirred at room temperature. After the polymerization was completed, cool MeOH was added. The product was isolated by precipitation in *n*-hexane followed by drying thoroughly in vacuum.

2. Experimental Data

2.1 The mechanism study of NHO1/TU1 system (In the absence of BnOH) ^a

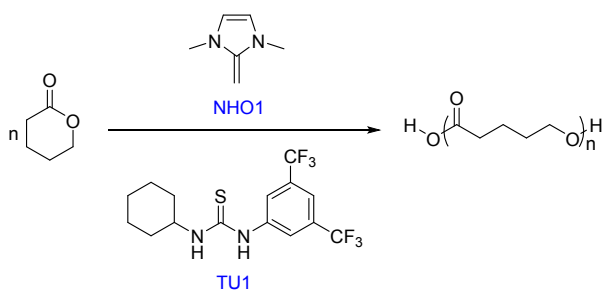


Table S1 NHO1/TU1 Catalytic System for ROP of δ -valerolactone

Entry	NHO1/TU1/BnOH/ δ -VL	Time/h	Conv./% ^b	<i>M_n</i> (kg/mol) ^c	<i>D</i> ^c
1	1:0:2:50	5	>99	4.9	1.78
2	1:2:0:50	5	>99	20.4	1.30
3	1:2:2:50	5	>99	4.0	1.23
4	1:1:0:20	5	>99	9.0	1.49
5	1:2:0:20	5	>99	14.7	1.33
6 ^d	1:1:0:5	12	>99	13.3	1.36
7 ^d	1:2:0:5	12	>99	15.5	2.11
8 ^e	2:4:0:50	4	29	13.4	1.20

^aConditions: room temperature, $n_{\text{monomer}} = 2.5$ mmol, toluene (0.5 mL) as the solvent. ^bMonomer conversion determined by ¹H NMR spectroscopy. ^c Number-average molecular weights (*M_n*) and polydispersity indices (*D*) determined by GPC analysis (THF). ^droom temperature, $n_{\text{monomer}} = 0.1$ mmol, toluene (0.5 mL) as the solvent. ^e $n_{\delta\text{-VL}} = 5$ mmol, toluene (1 mL) as the solvent, H₂O as the initiator, NHO1:TU:H₂O:M = 2:4:1:50.

The experimental results are summarized in Table S1. In the absence of TU1, the monomer conversion was > 99% and M_n was 4900 (entry 1). Without BnOH, comparatively high conversion of 99% was observed with NHO1/TU1 ratio of 1:2 (entry 2). M_n value improved from 4900 to 20400 g/mol. When the amount of monomer is reduced from 50 to 20, the molecular weight is still very high (entry 4, 5). While the amount of monomer is reduced to 5, the molecular weight can still reach 15500 (entry 7). When water is used instead of benzyl alcohol as an initiator, a conversion of 29% can be achieved in 4 hours, and the molecular weight is still high (entry 8). The above experimental results indicated that trace amount of water may be used as initiator in NHO1/TU1 system. ^1H NMR spectra (Figure S1) of the obtained PVL can also verify this speculation.

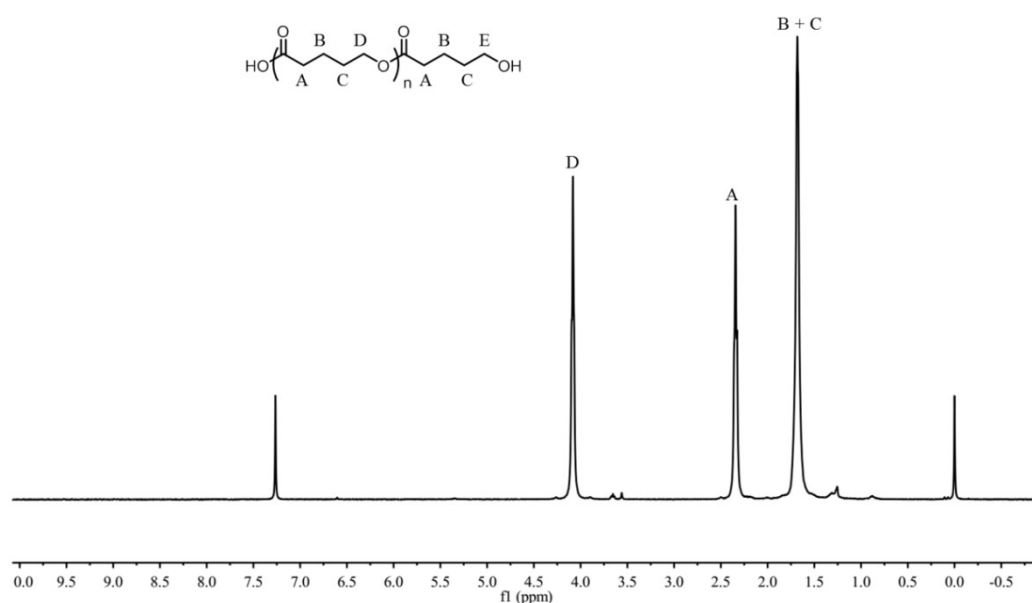


Figure S1. ^1H NMR spectra of the obtained PVL in CDCl_3 . The polymer (NHO1:TU1: BnOH: δ -VL = 1:2:0:5) was isolated by reprecipitation from toluene in cold methanol.

2.2 NHO/TU Catalytic System for ROP of δ -valerolactone

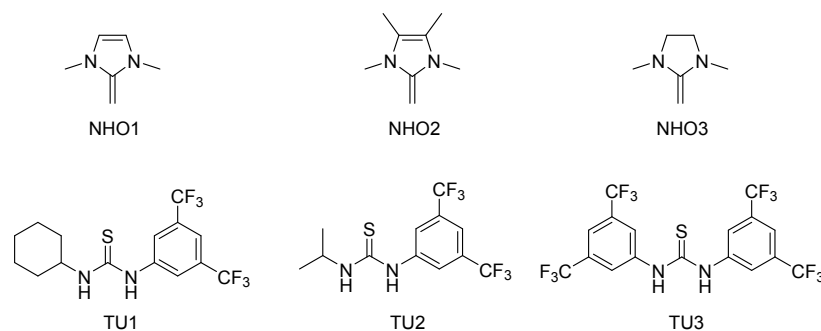


Table S2 Optimization of conditions (NHO2/TU1)^a

Entry	NHO2/TU1/BnOH/ δ -VL	Time/h	Conv./% ^b	<i>M_n</i> (kg/mol) ^c	<i>D</i> ^c
1	1:1:2:100	12	97	6.3	1.12
2	1:1:0:100	12	34	11.0	1.16
3	1:0:2:100	12	42	3.6	1.15
4	1:0:0:100	12	3	--	--
5	1:2:2:100	4	95	6.1	1.12

^aConditions: room temperature, $n_{\text{monomer}} = 5$ mmol, toluene (1 mL) as the solvent. ^bMonomer conversion determined by ¹H NMR spectroscopy. ^c Number-average molecular weights (*M_n*) and polydispersity indices (*D*) determined by GPC analysis (THF).

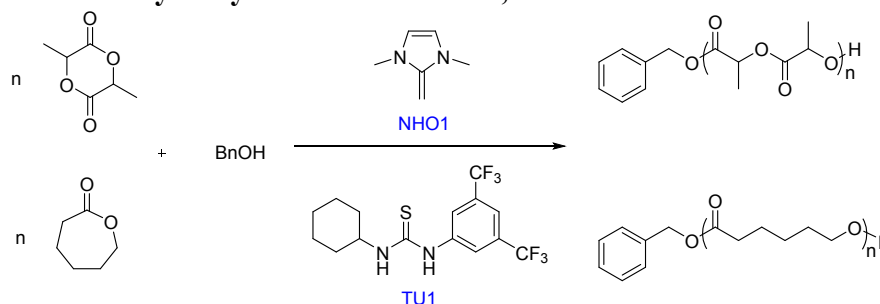
Table S3 ROP of δ -VL using different NHOs and TUs^a

Entry	NHO/TU/BnOH/ δ -VL	Time/h	Conv./% ^b	<i>M_n</i> (kg/mol) ^c	<i>D</i> ^c
1	NHO1/TU1/BnOH/ δ -VL = 1:2:2:100	4	97	6.3	1.21
2	NHO1/TU1/BnOH/ δ -VL = 1:2:2:200	24	49	5.1	1.13
3	NHO1/TU1/BnOH/ δ -VL = 1:1:0:100	12	52	12.5	1.28
4	NHO1/TU1/BnOH/ δ -VL = 1:2:0:100	7	48	9.8	1.36
5	NHO1/TU2/BnOH/ δ -VL = 1:2:2:100	7	97	6.5	1.13
6	NHO1/TU2/BnOH/ δ -VL = 1:1:0:100	7	49	8.6	1.34
7	NHO1/TU3/BnOH/ δ -VL = 1:2:2:100	12	trace	--	--
8	NHO2/TU1/BnOH/ δ -VL = 1:1:2:100	12	97	6.3	1.12
9	NHO2/TU1/BnOH/ δ -VL = 1:2:2:100	4	95	6.1	1.12
10	NHO2/TU1/BnOH/ δ -VL = 1:1:0:100	12	34	11.0	1.16
11	NHO2/TU1/BnOH/ δ -VL = 1:2:0:100	12	18	5.9	1.18
12	NHO2/TU2/BnOH/ δ -VL = 1:2:2:100	7	95	6.6	1.11
13	NHO2/TU2/BnOH/ δ -VL = 1:1:0:100	7	19	6.4	1.20
14	NHO2/TU3/BnOH/ δ -VL = 1:2:2:100	7	trace	--	--
15	NHO3/TU1/BnOH/ δ -VL = 1:2:2:100	4	93	6.7	1.11
16	NHO3/TU1/BnOH/ δ -VL = 1:1:0:100	12	5	--	--

17	NHO3/TU2/BnOH/ δ -VL = 1:2:2:100	12	62	3.8	1.10
18	NHO3/TU2/BnOH/ δ -VL = 1:1:0:100	12	7	--	--
19	NHO3/TU3/BnOH/ δ -VL = 1:2:2:100	4	trace	--	--

^aConditions: room temperature, $n_{\text{monomer}} = 5$ mmol, toluene (1 mL) as the solvent. ^bMonomer conversion determined by ¹H NMR spectroscopy. ^c Number-average molecular weights (M_n s) and polydispersity indices (D) determined by GPC analysis (THF).

2.3 NHO/TU Catalytic System for ROP of D, L-LA and ϵ -CL ^a



Typical procedure for polymerization of D, L-LA

In an Ar-filled glovebox, the catalysts of NHO (0.04 mmol, 0.01 eq.), TU (0.08 mmol, 0.02 eq.) and initiator of BnOH (0.08 mmol, 0.02 eq.) were dissolved into 2 mL THF in Schlenk tube. Then 0.29 g δ -VL (2 mmol, 50 eq.) was added to the mixture solution. The reaction mixtures were stirred at room temperature. After the polymerization was completed, cool MeOH was added. The product was isolated by precipitation in *n*-hexane followed by drying thoroughly in vacuum.

Typical procedure for polymerization of ϵ -CL

In an Ar-filled glovebox, the catalysts of NHO (0.05 mmol, 0.01 eq.), TU (0.1 mmol, 0.02 eq.) and initiator of BnOH (0.1 mmol, 0.02 eq.) were dissolved into 1 mL toluene in Schlenk tube. Then 0.55 mL δ -VL (5 mmol, 100 eq.) was added via a syringe to the mixture solution. The reaction mixtures were stirred at room temperature. After the polymerization was completed, cool MeOH was added. The product was isolated by precipitation in *n*-hexane followed by drying thoroughly in vacuum.

Table S4 ROP of D, L-LA and ϵ -CL

Entry	Monomer	NHO1/TU1/BnOH/M	Time	Conv./% ^b	M_n /(g/mol) ^c	D ^c
1 ^a	D,L-LA	1:2:2:200	10 min	>99%	19.7	1.44

2 ^a	D,L-LA	1:2:1:200	10 min	>99%	26.0	1.60
3 ^a	D,L-LA	1:2:2:500	4 h	33	24.4	1.14
4 ^d	ϵ -CL	1:2:2:100	24 h	33	2.8	1.11

^aConditions: room temperature $n_{\text{monomer}} = 2$ mmol, toluene (2 mL) as the solvent. ^bMonomer conversion determined by ¹H NMR spectroscopy. ^c Number-average molecular weights (M_n) and polydispersity indices (\mathcal{D}) determined by GPC analysis (THF). ^d $n_{\text{monomer}} = 5$ mmol, toluene (1 mL) as the solvent.

3. Spectral Data

3.1 GPC Data

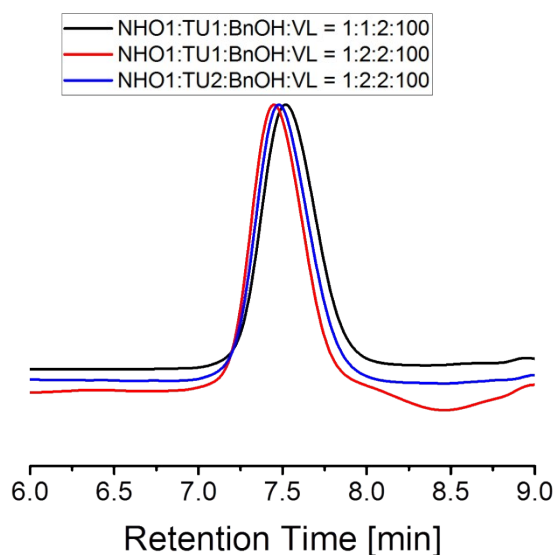


Figure S2. GPC traces for PVL (black, NHO1:TU1:BnOH: δ -VL = 1:1:2:100, $M_n = 6000$, $\mathcal{D} = 1.12$; red, NHO1:TU1:BnOH: δ -VL = 1:2:2:100, $M_n = 6300$, $\mathcal{D} = 1.21$; blue, NHO1:TU2:BnOH: δ -VL = 1:1:2:100, $M_n = 6500$, $\mathcal{D} = 1.13$) produced by NHO/TU/BnOH in toluene at room temperature. As can be seen from figure S2, the molecular weight distributions estimated by the GPC measurement were relatively low.

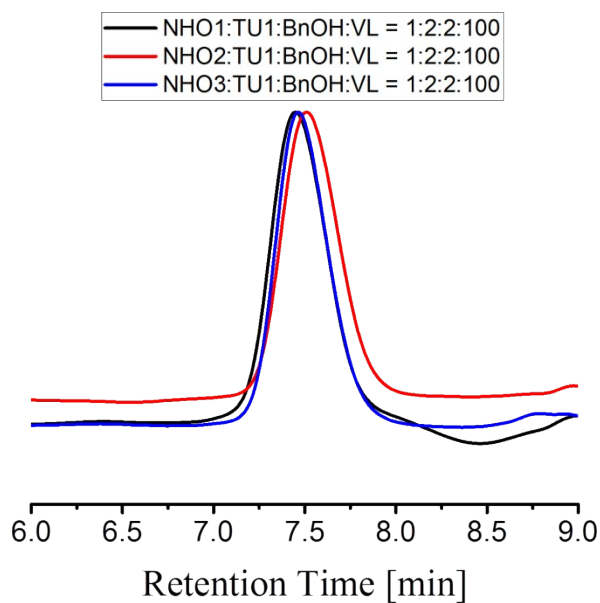


Figure S3. GPC traces for PVL (black, NHO1: δ -VL = 1:100, M_n = 6300, \bar{D} = 1.21; red, NHO2: δ -VL = 1:100, M_n = 6900, \bar{D} = 1.12; blue, NHO3: δ -VL = 1:100, M_n = 6700, \bar{D} = 1.11) produced by NHO/TU1/BuOH = 1:2:2 in toluene at room temperature. As can be seen from figure S3, the molecular weight distributions estimated by the GPC measurement were relatively low.

3.2 ^1H NMR Data

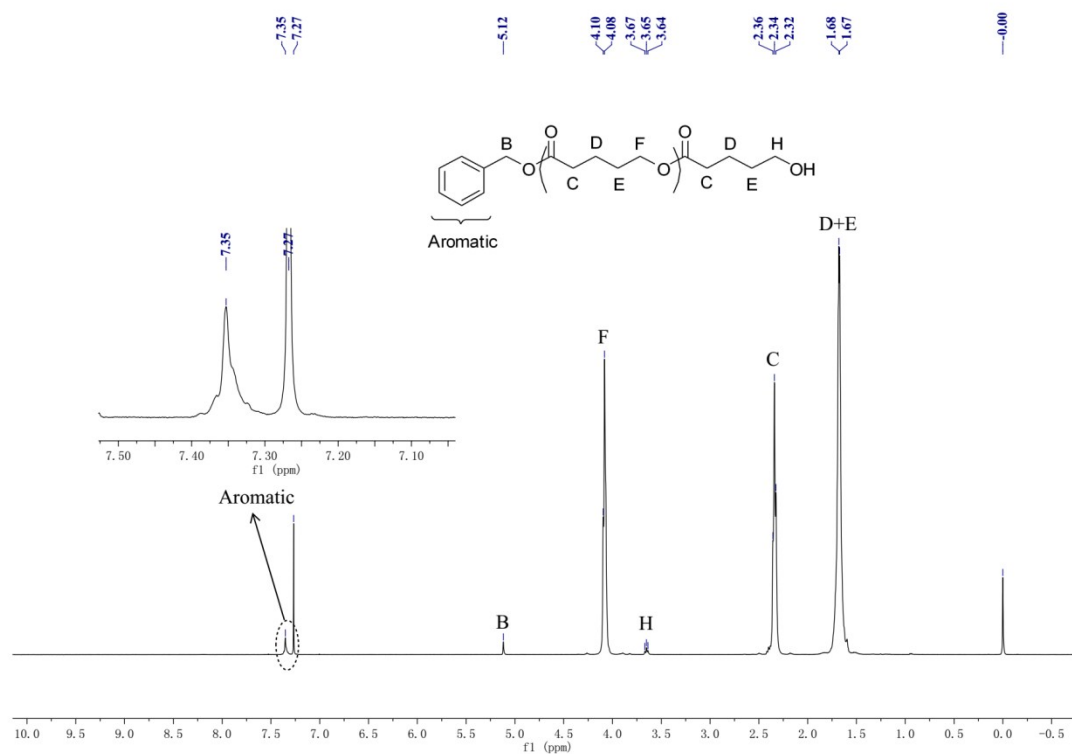


Figure S4. ^1H NMR spectra of the obtained PVL in CDCl_3 . The polymer (NHO1:TU1:BuOH: δ -VL = 1:2:2:100) was isolated by reprecipitation from toluene in cold methanol. ^1H NMR (400 MHz,

CDCl₃) δ (ppm) 7.37-7.32 (m, 5H, Aromatic), 5.12 (s, 2H, ArCH₂-), 4.10-4.08 (t, 2H \times n, $J = 8.0$ Hz, (-CH₂CH₂O-)n), 3.67-3.64 (t, 2H, $J = 12.0$ Hz, -CH₂CH₂OH), 2.36-2.32 (t, 2H \times n, $J = 16.0$ Hz, (-OCOCH₂CH₂-)n), 1.68 (m, 2H \times n, (-COCH₂CH₂CH₂-)n), 1.67 (m, 2H \times n, (-CH₂CH₂CH₂O-)n). In the ¹H NMR spectrum (Figure S4), the peak centered around 7.4 ppm with relative peak area of 5, was ambiguously assigned to the BnO group.

3.3

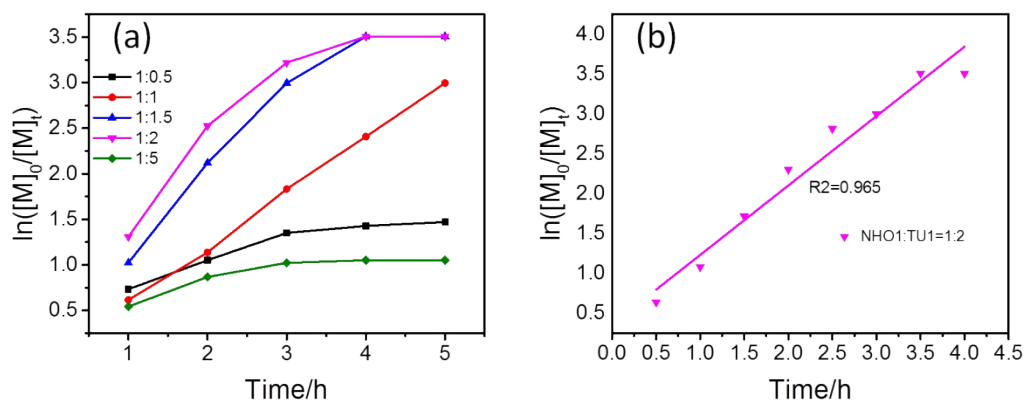


Figure S5. (a) Plots of $\ln([M]_0/[M]_t)$ versus reaction time for the different ratio of NHO1 and TU1 - catalyzed AROPs under the conditions of $[NHO1]_0/[BnOH]_0/[M]_0 = 1/2/100$, (b) Plots of $\ln([M]_0/[M]_t)$ versus reaction time (0.5 h - 4 h) under the conditions of $[NHO1]_0/[TU1]_0/[BnOH]_0/[M]_0 = 1/2/2/100$. $M = \delta$ -VL.