# Electronic Supporting Information

# Green and sustainable synthesis of poly(δ-valerolactone) with TBD catalyzed ring-opening polymerization reaction

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## 1. Experimental equipment of batch reaction

The batch reactors used for the $CO_2$ quenching experiments and PVL precipitation experiments are shown in Fig. S1. The volume of the bottle reactor was 20 mL, and reaction temperature was controlled by a heating mode equipped with a temperature sensor on the magnetic stirrer. $CO_2$ was fed into the solution from a needle on the top of the bottle, and another needle was used as the gas phase outlet to balance the pressure.

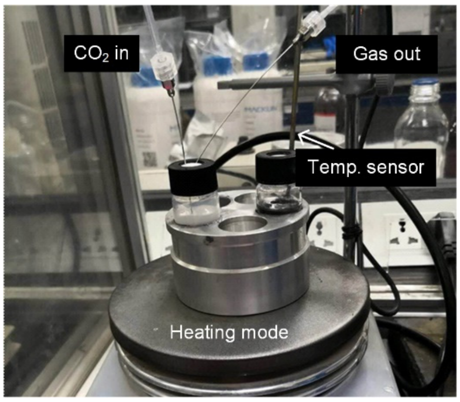

**Fig. S1** Photo of batch reaction equipment.

## 2. Flow ROP reactor platform

The flow ROP reaction was implemented via the tubular reactor platform as shown in Fig. S2(a). The platform was assembled by syringe pumps with gas-tight syringes for TBD + BnOH solution, δ-valerolactone solution, and flush toluene, three-way switching valves, $CO_2$ gas flow controller, Y-junction connectors, FEP tubes, and constant-temperature water bath. A home-made screw tube mixer shown in Fig. S2(b) was used to mix the TBD + BnOH solution and δ-valerolactone solution. The screw tube mixer was made from a 1.6 mm out-diameter FEP tube via thermoforming method reported in our previous paper [1].

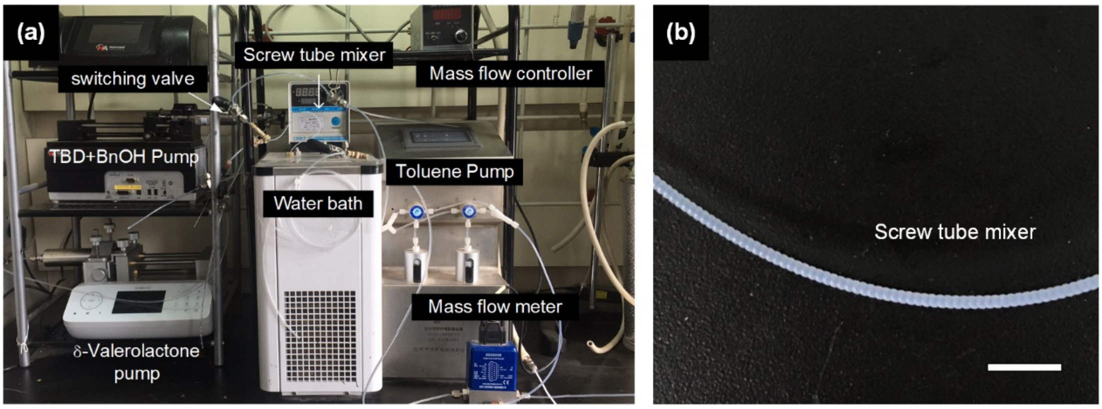

**Fig. S2** Flow ROP reaction platform. (a) Photo of the entire platform; (b) Photo of the screw tube mixer. The scale bar shows 1 cm.

## 3. Distillation simulation with Aspen Plus

A virtual input flow with a mixture of 32.96 kg/h n-hexane, 10.58 kg/h toluene, and 0.32 kg/h δ-valerolactone, which had the similar composition as the residual solution after PVL precipitation, was fed into the model column with 9 stages as shown by Fig. S3. Aspen Plus 8.4 was employed to simulate the distillation results. The mixture of n-hexane, toluene, and δ-valerolactone was fed from the 5th stage and the molar reflux ratio was 3. Parameter details in the simulation are given in Table S1.

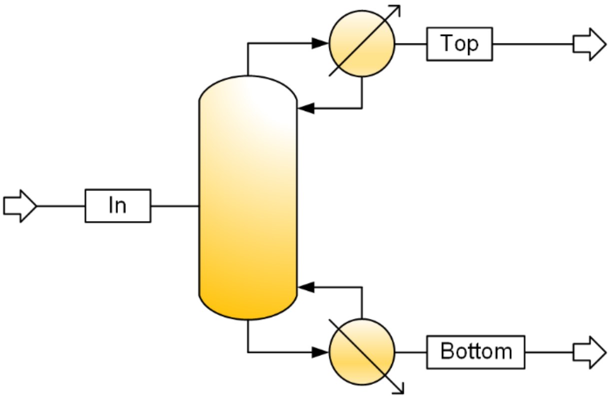

**Fig. S3** Schematic of the model distillation column.

**Table S1** Input and output streams of the distillation column

| | In | Bottom | Top |
|---|---|---|---|
| Temperature (°C) | 90 | 110.5 | 68.7 |
| Pressure (bar) | 2 | 1 | 1 |
| N-hexane (kmol/h) | 3.758E-1 | 8.050E-4 | 3.749E-1 |
| Toluene (kmol/h) | 1.206E-1 | 1.136E-1 | 7.034E-3 |
| δ-valerolactone (kmol/h) | 3.648E-3 | 3.648E-3 | trace |
| Total mole flow (kmol/h) | 0.500 | 0.118 | 0.382 |

| | | | |
|---|---|---|---|
| Total mass flow (kg/h) | 43.86 | 10.9 | 32.96 |
| Volume flow ($m^3$/h) | 0.063 | 0.014 | 0.053 |
| Enthalpy (gcal/h) | -0.018 | < 0.001 | -0.017 |

## 4. PVL polydispersity indexes (PDI) at different δ-valerolactone conversion.

The PDIs of PVL in different TBD catalyzed ROP reactions in the control experiment are shown in Fig. S4. This figure exhibits that when the monomer conversion gets higher than 95%, the PDI starts to increase greatly. The result is in accordance with the study for lactide ROP from Zuilhof et al. [2]

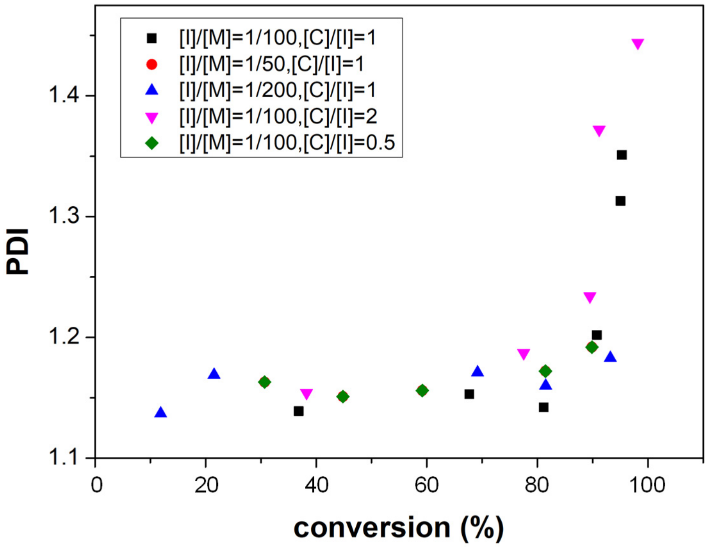

**Fig. S4** Variation of PDI of PVL with δ-valerolactone conversion. [I], [M], and [C] show the initial concentrations of initiator BnOH, monomer δ-valerolactone, and catalyst TBD, respectively.

## 5. Typical $^1$H-NMR spectra of chemicals

Standard spectra of PVL and δ-valerolactone are shown by Figs. S5 and S6, respectively. Figs. S7 and S8 show the spectra of TBD and TBD solution in toluene, respectively. Figs. S9 and S10 show the spectra of the bicarbonate of TBD from the reaction of TBD and $CO_2$ and the residual solution after centrifugal separation of TBD-$CO_2$ adduct. Fig. S11 shows the spectrum of TBD solution after removing $CO_2$ by heating to 70 °C, which is almost the same as that in Fig. S8. Fig. S12 shows the spectrum of the solid precipitated from the mixture of n-hexane and the quenched production solution, indicating that the solid was composed by PVL and TBD. Fig. S13 shows the spectrum of the residual solution after centrifugal separation of the solid phase in the mixture of n-hexane and the quenched production solution, indicating that the solution was composed by n-hexane, toluene and δ-valerolactone only, which did not contained TBD and PVL. Fig. S14 shows the spectrum of the precipitated solid after water washing, which indicates that the solid was PVL only.

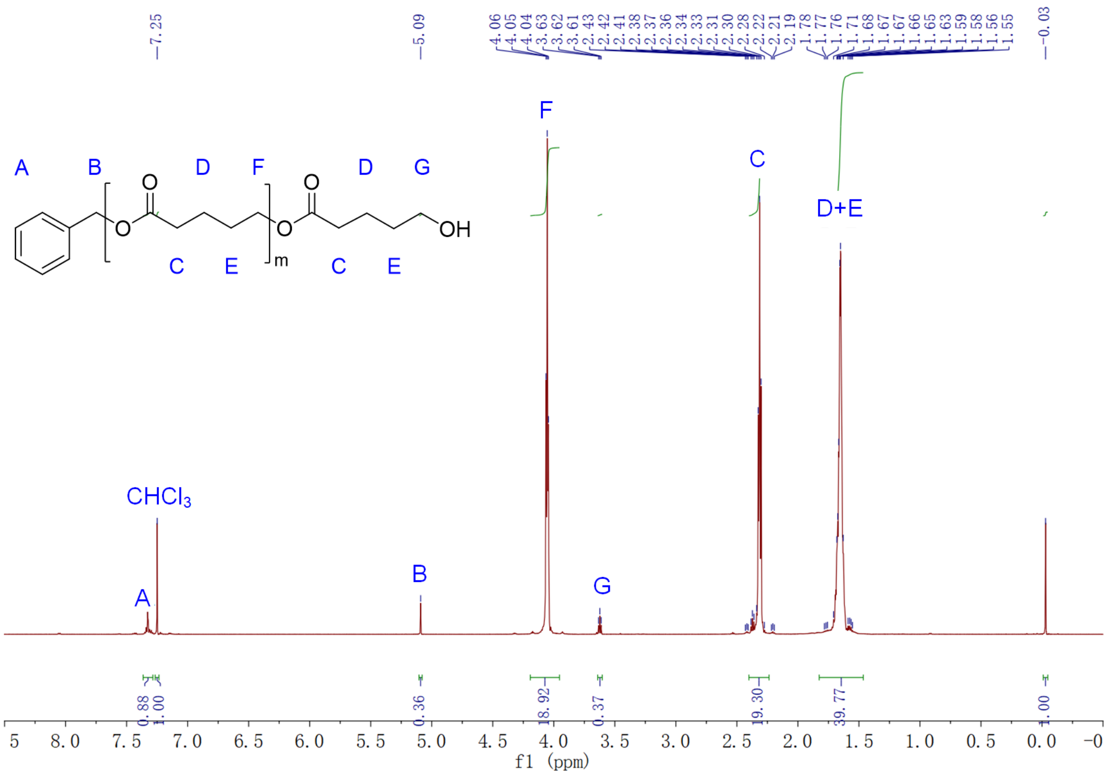

**Fig. S5** $^1$H-NMR spectrum of PVL.

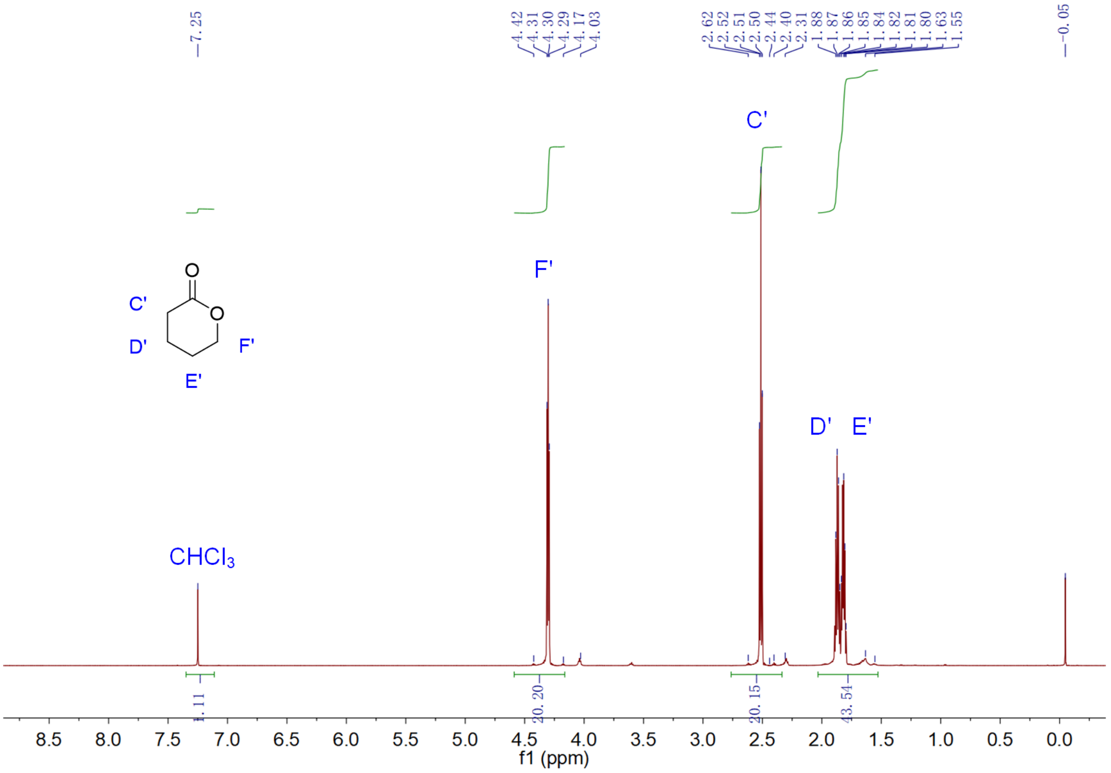

**Fig. S6** $^1$H-NMR spectrum of δ-valerolactone.

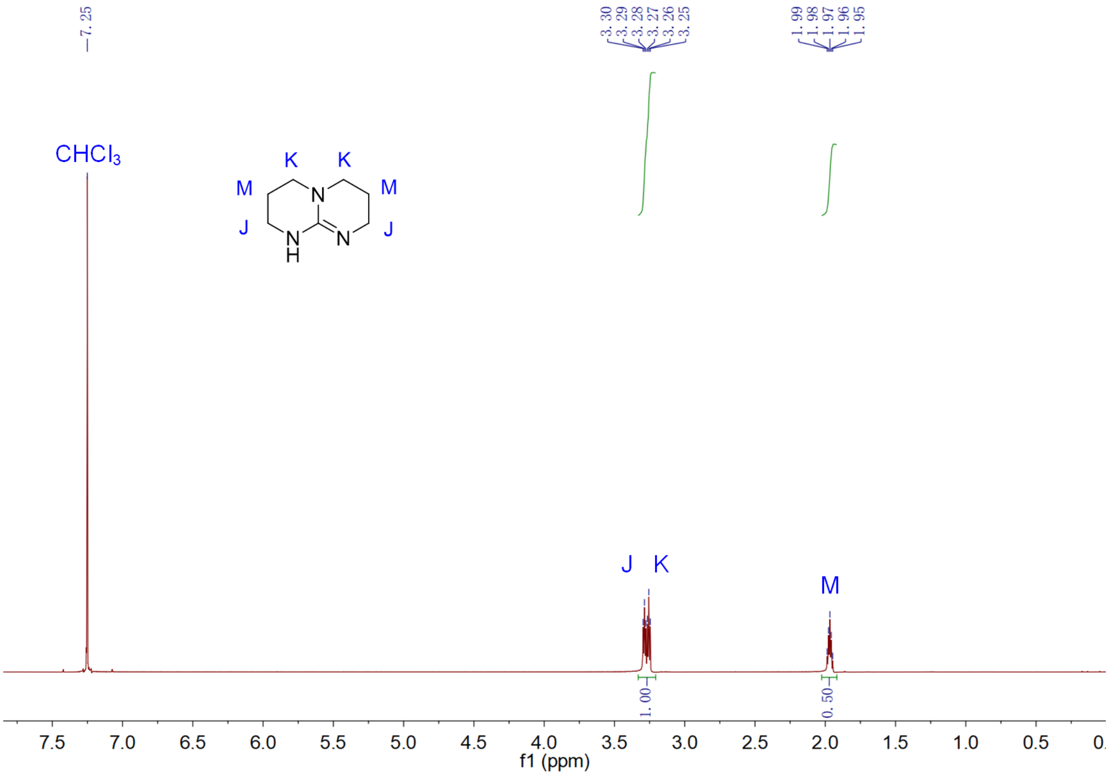

**Fig. S7** $^1$H-NMR spectrum of TBD.

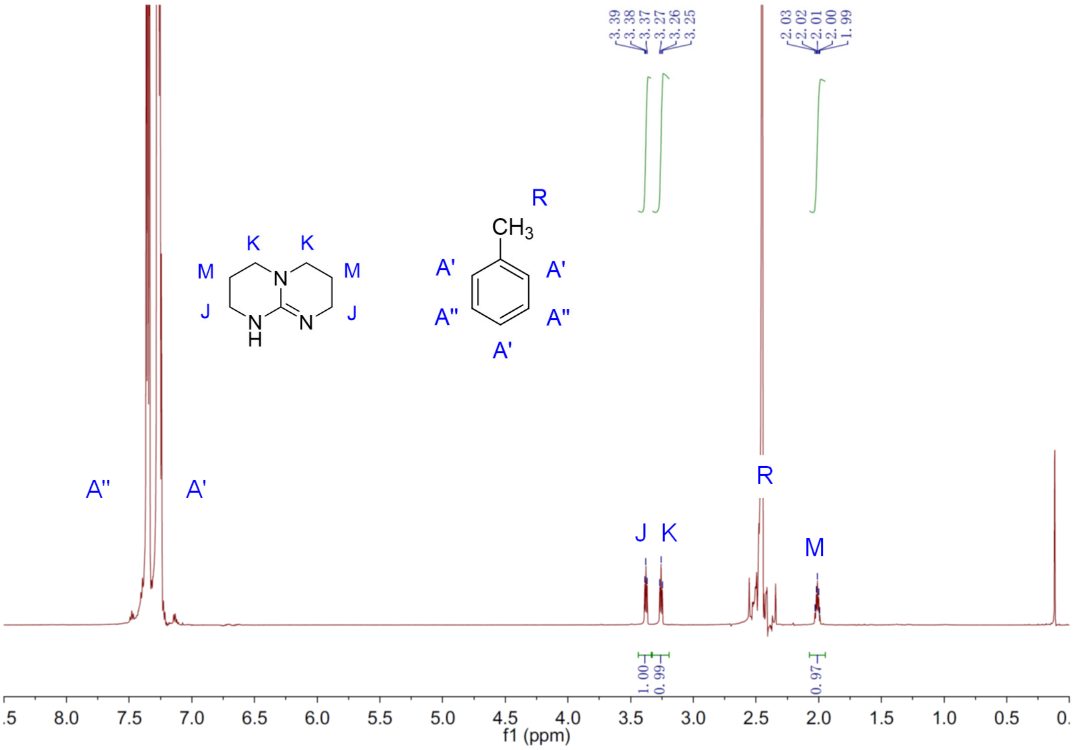

**Fig. S8** $^1$H-NMR spectrum of TBD solution in toluene. [TBD] = 0.04 mol/L

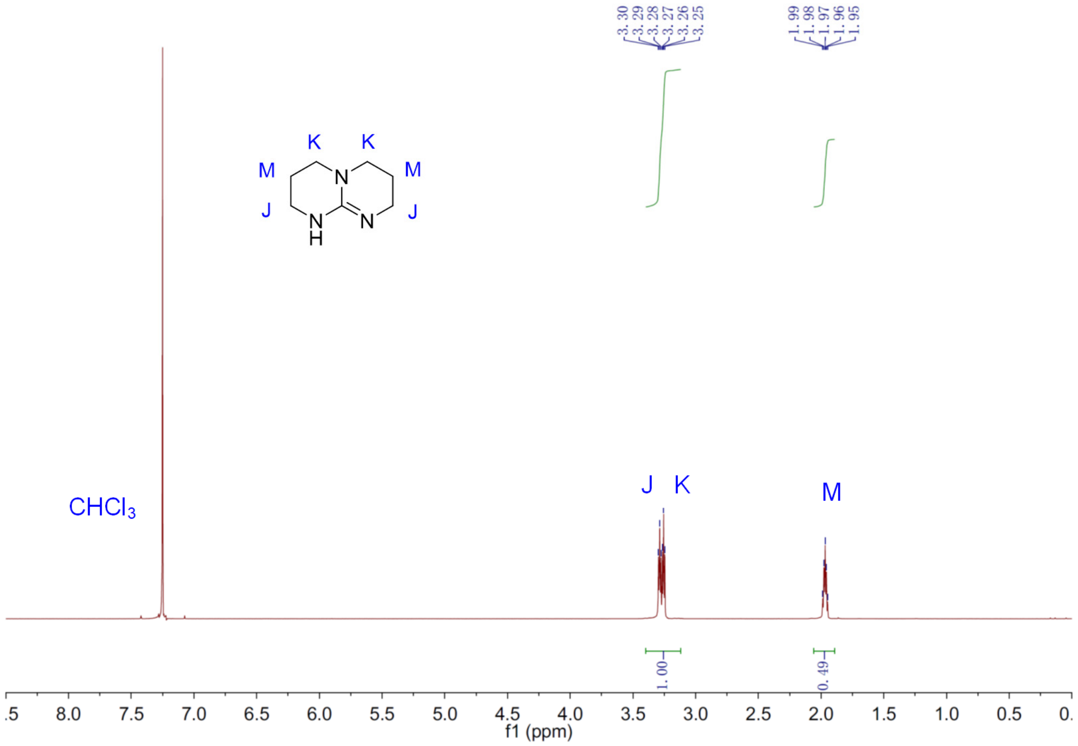

**Fig. S9** ${}^1$H-NMR spectrum of the white solid from the reaction of TBD and $CO_2$ in toluene.

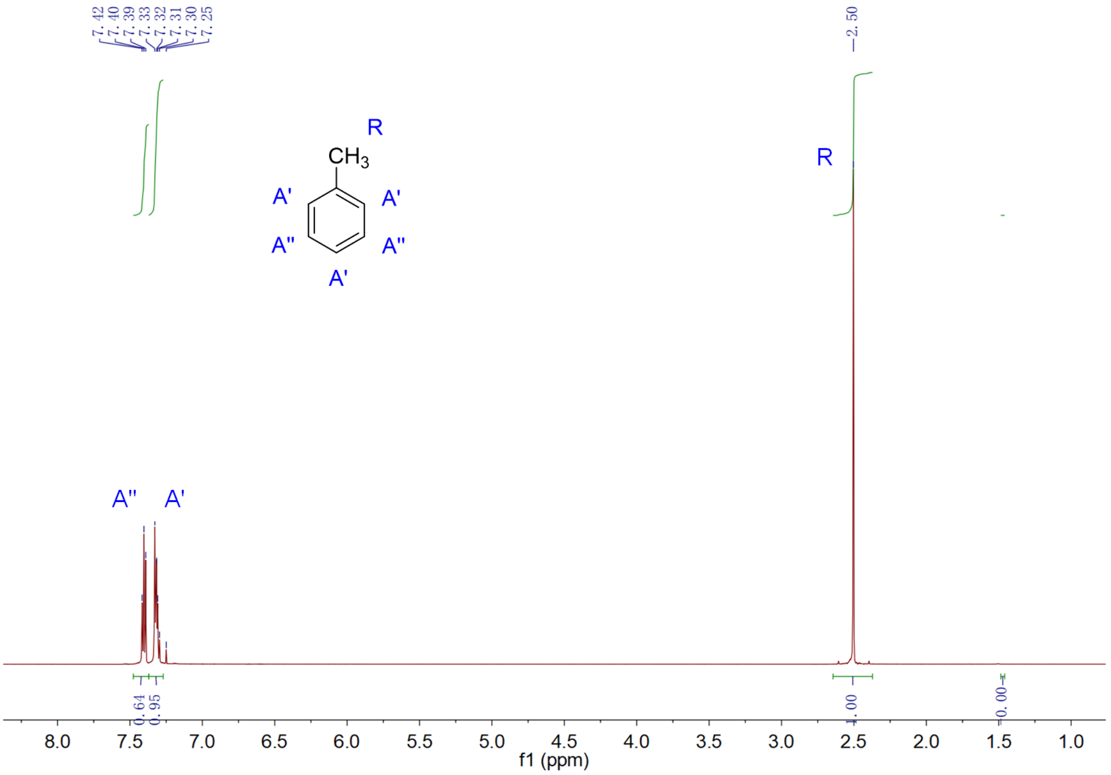

**Fig. S10** ${}^1$H-NMR spectrum of the remaining solution from the reaction of TBD and $CO_2$ in toluene after centrifugal separation of the solid in Fig. S9.

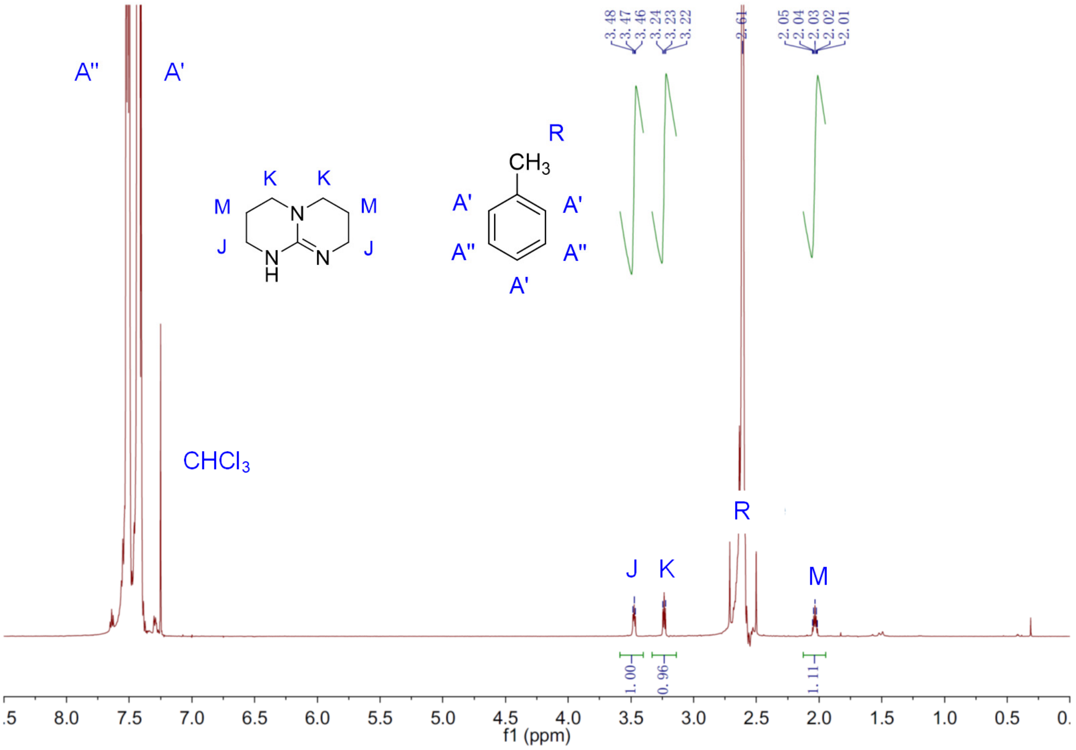

**Fig. S11** $^1$H-NMR spectrum of TBD solution after heating to remove $CO_2$ at 70 ℃. [TBD] = 0.04 mol/L.

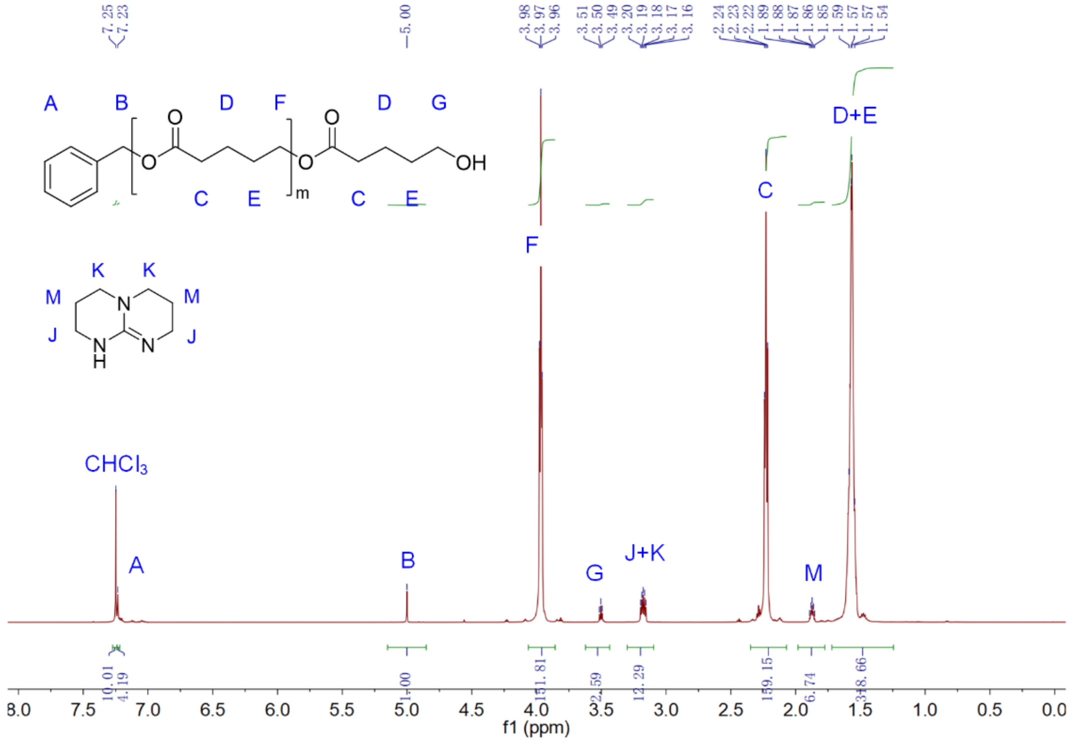

**Fig. S12** $^1$H-NMR spectrum of the white solid from the precipitation experiment of PVL. Experiment started with $[VL]_0$ = 2 mol/L, $[TBD]_0$ = 0.04 mol/L, and $[BnOH]_0$ = 0.04 mol/L. Product PVL had 5100 g/mol $M_{n,NMR}$ and 1.12 PDI.

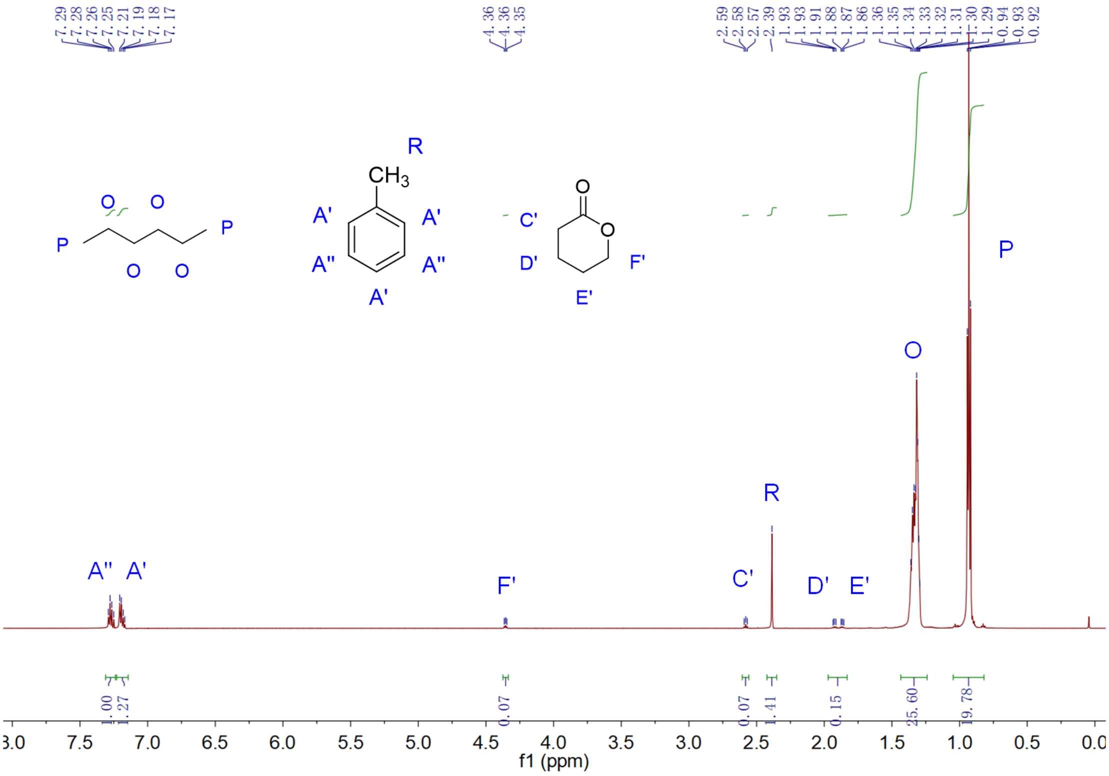

**Fig. S13** $^1$H-NMR spectrum of the residual liquid from the precipitation experiment.

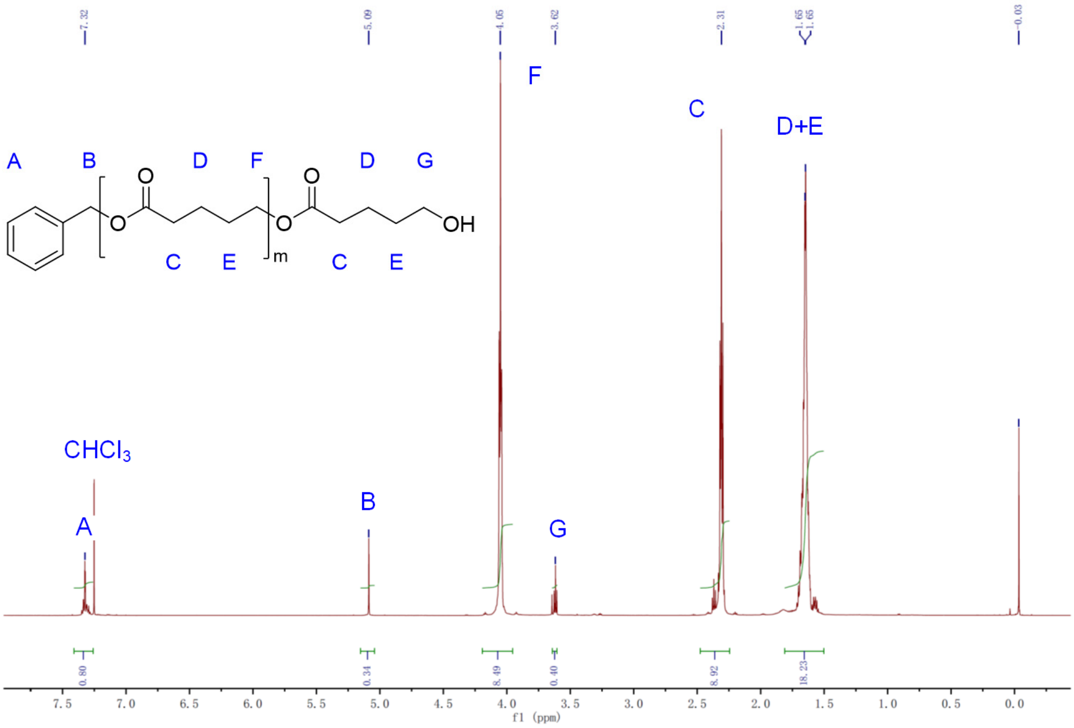

**Fig. S14** $^1$H-NMR spectrum of the solid after water washing.

## References

1. K. Wang, H. Zhang, Y. Shen, A. Adamo and K. F. Jensen, *React Chem Eng*, 2018, **3**, 707-713.
2. S. A. van den Berg, H. Zuilhof and T. Wennekes, *Macromolecules*, 2016, **49**, 2054-2062.