Electronic Supporting Information

Kinetic study of TBD catalyzed δ-valerolactone polymerization via a gas-driven droplet flow reactor

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Experimental Platform

The gas-driven droplet reactor system is shown in Fig. S1(a). The left part of the platform was feeding pumps of δ-valerolactone (δ-VL) solution, TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) and benzyl alcohol (BnOH) mixture solution, and benzoic acid (BA) solution (PHD Ultra 70-3310C, Harvard Apparatus). The right part of the platform was the 6-way valve (Idex Health & Science), the fluoroplastics reaction tubes, water bath (Beijing Hengtai), the gas feed system (Sevenstar), and the feeding pump of washing toluene (PPI, Hangzhou China). Fig. S1(b) shows some details near the 6-way valve. A droplet in the outlet tube is indicated. Fig. S1(c) is a photo of the screw tube mixer,[1] which inner structure is shown by a microscope picture.

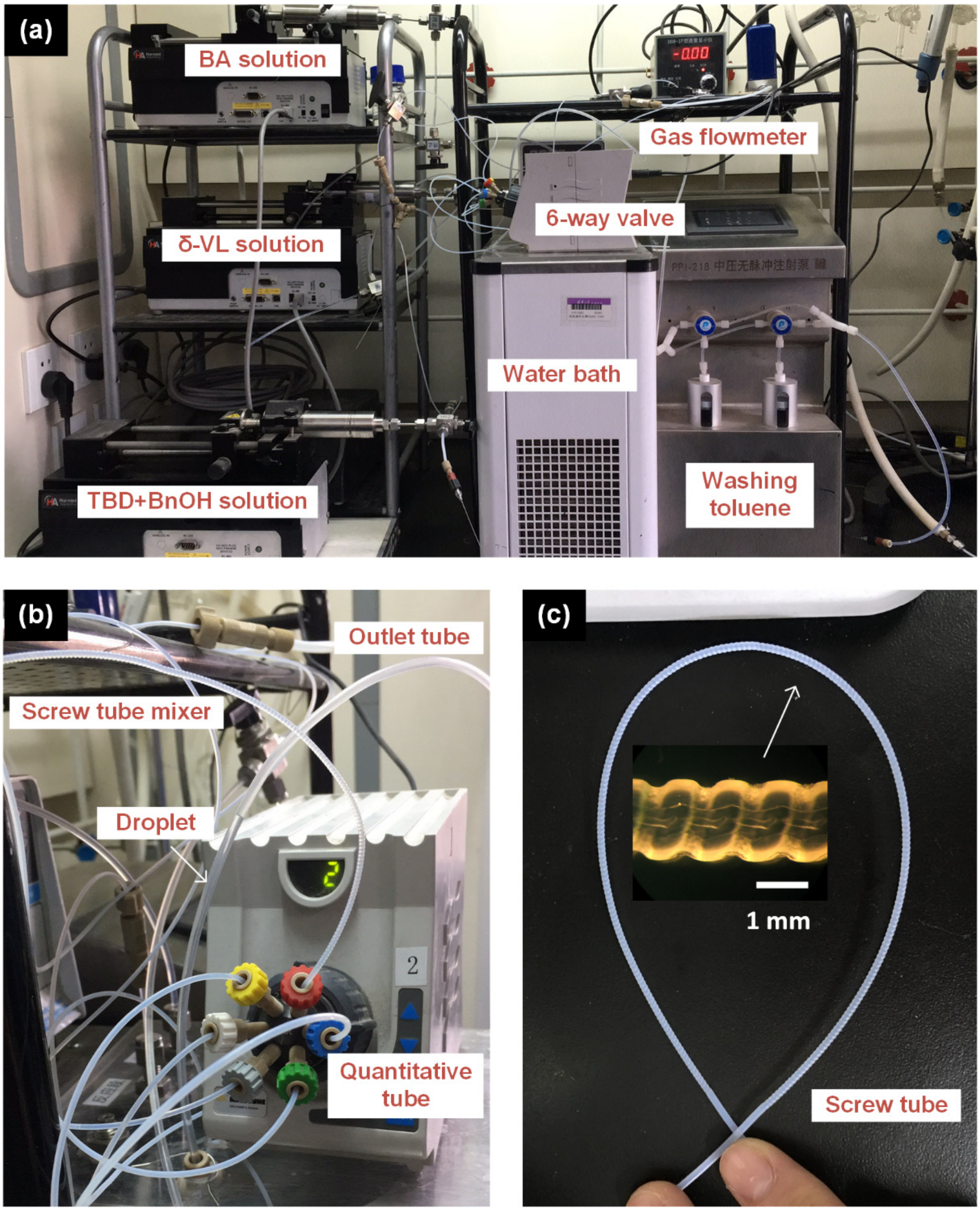

Fig. S1 Photos of the gas-driven droplet reactor system

(a) The experimental platform; (b) The 6-way valve and the tubes; (c) Photos of the screw tube mixer. Some assistant valves are not shown in the main text, Fig. 1, for clear exhibition.

^{1}H NMR analysis

The δ-valerolactone conversion and the average molecule weight were analyzed by ^{1}H-NMR (JNM-ECA600, 600 MHz, Chloroform-*d*). Fig. S2(a) shows a spectrum of PVL product. The peaks are 1.83 – 1.46 (m, $-CH_2C\underline{H}_2C\underline{H}_2CH_2OCO-$), 2.31 (t, $-C\underline{H}_2CH_2CH_2CH_2OCO-$), 3.62 (t, $-C\underline{H}_2OH$), 4.06 (s, $-CH_2CH_2CH_2C\underline{H}_2OCO-$), 5.09 (s, $ArC\underline{H}_2O-$), and 7.33 (s, aromatic). Fig. S2(b) shows a spectrum of δ-VL. The peaks are 2.03 – 1.53 (m, $-CH_2C\underline{H}_2C\underline{H}_2CH_2OCO-$), 2.51 (t, $-CH_2CH_2CH_2C\underline{H}_2OCO-$), 4.59 – 4.16 (m, $-C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_2OCO-$).

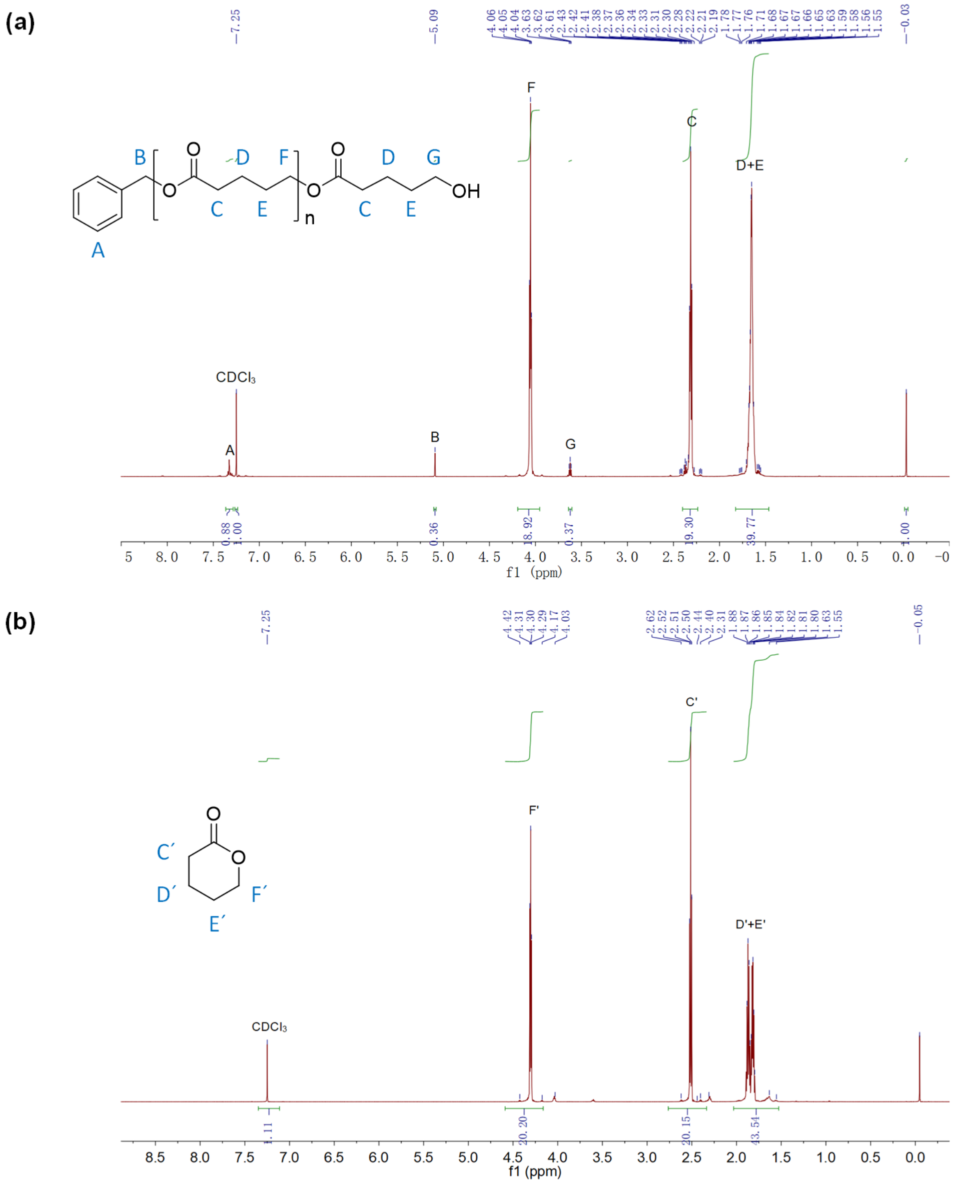

Fig. S2 ^{1}H-NMR spectra of PVL and δ-VL.

The corresponding molecular structure of the peaks are shown in the figures.

Using the peak area ratio, the VL conversion was calculated as

$$x = (F+G)/(F+G+F') \tag{S1}$$

And the number-average molecular weight $M_{n,NMR}$ was obtained from the peak area ratio of $(F+G)/B$.

$$M_{\mathrm{n,NMR}} = M_{\mathrm{BnOH}} + M_{\mathrm{VL}}\left(\frac{F+G}{B}\right) \qquad \text{(S2)}$$

in which M_{BnOH} and M_{VL} are molecular weights of benzyl alcohol and δ-valerolactone, respectively.

GPC analysis

Gel permeation chromatography (GPC) analysis was used to determine the molecule weight distribution of PVL products. A Waters GPC system equipped with 2707 autosampler, 1515 HPLC pump, 2414 refractive index detector, and 3 styragel columns (HR1, HR2 and HR3 at 30 ºC). THF was used as the eluent at a flow rate of 1 mL/min. The standards used to calibrate the polymer molecule weight was polystyrene (SHODEX SL-105 STANDARD) with molecule weight range from 610~20300 g/mol, which covered the molecule weights of PVL (from about 2000 to 15000 g/mol). Some typical spectra of the PVL products during the experiments are shown in Fig. S3.

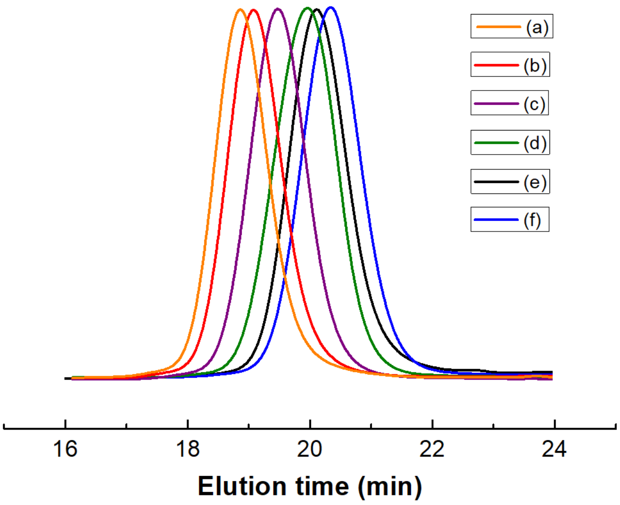

Fig. S3 GPC spectra of PVL products.

The experimental conditions are $[VL]_0$ = 1 mol/L, $[TBD]_0$ = 0.005 mol/L, and $[BnOH]_0$ = 0.01 mol/L at T = 30ºC. (a) to (f) represent Samples 1 to 6 in Table 1.

References

1. K. Wang, H. Zhang, Y. Shen, A. Adamo and K. F. Jensen, *React Chem Eng*, 2018, **3**, 707-713.