Electronic Supplementary Information (ESI) for

o-Benzenedisulfonimide as a recyclable cationic organocatalyst for the controlled/living ring-opening polymerization of δ valerolactone and ε -caprolactone[†]

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Preparation of o-Benzenedisulfonimide (OBS)

1.0 g *o*-benzenedisulfonyl chloride was dissolved in 20 ml dry toluene. Then NH₃/EtOH (3.1g NH₃ gas in 50 ml of EtOH) was dropwise added at 0 °C followed by filtered and evaporated under vacuum. The residue mixture was dissolved in water, and then filtered out yielded solid bisamide. With a final purification of the filtrate by cationic exchange (Dowex resin 50 \times 8-100, 30g), 0.51 g white solid was obtained. Anhydrous imide by boiling down toluene soln and cooling, crystals, mp 193-194 °C. 500 mg, 67% yield;

¹H NMR (300 MHz, DMSO- d_6 , δ): 7.58-7.884 (m), 10.44 (s).

¹³C NMR (300 MHz, DMSO, *δ*): 142.41 (s), 132.31 (s), 120.76 (s)

H RMS (ESI-) (m/z): [M - H]⁻ calculated for C₆H₅NO₄S₂, 218.97; found, 217.96.

The Recycling Process of o-Benzenedisulfonimide

After separating polymers from cold methanol, the residue solution was evaporated under vacuum followed by an addition of Et_2O and H_2O (1:1, 10 mL). The aqueous layer was collected and passed through a column of Dowex 50X8 ion-exchange resin. Then OBS was recrystallized from toluene to give white needles crystal (over 90%, yield). The recovered OBS could be reused as a catalyst again.



Fig. S1 Mass spectrum of o-benzenedisulfonimide.



Fig. S2 ¹H NMR spectrum of *o*-benzenedisulfonimide.



Fig. S3. ¹³C NMR spectrum of *o*-benzenedisulfonimide.







Fig. S5 ¹H NMR spectrum of PCL-*b*-PVL initiated from BnOH in CDCl₃.



Fig. S6 SEC traces of the resulting PVL initiated by H₂O.







Fig. S8 ¹³C NMR spectra of the carbonyl carbon signals of (a) δ -VL in CD₂Cl₂, (b) a 1 : 1 mixture of δ -VL and OBS in CD₂Cl₂, (c) δ -VL in Toluene-d8, (d) a 1:1 mixture of OBS and δ -VL in Toluene-d8.



Fig. S9 ¹³C NMR spectra of the carbonyl carbon signals with various ratios of 0, 0.2:1, 0.3:1, 0.6:1, 0.8:1, 1:1, 1.5:1, 2:1 between OBS and δ -VL.