Electronic Supplementary Information (ESI) for

\textit{o-Benzenedisulfonimide as a recyclable cationic organocatalyst for the controlled/living ring-opening polymerization of $\delta$-valerolactone and $\epsilon$-caprolactone}†

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\textbf{Preparation of \textit{o-Benzenedisulfonimide (OBS)}}

1.0 g \textit{o-benzenedisulfonyl chloride} was dissolved in 20 ml dry toluene. Then \textit{NH$_3$/EtOH} (3.1g \textit{NH$_3$ 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 × 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;

$^1$H NMR (300 MHz, DMSO-$d_6$, $\delta$): 7.58-7.884 (m), 10.44 (s).

$^{13}$C NMR (300 MHz, DMSO, $\delta$): 142.41 (s), 132.31 (s), 120.76 (s)

H RMS (ESI-) ($m/z$): [M - H] calculated for C$_6$H$_5$NO$_4$S$_2$, 218.97; found, 217.96.

\textbf{The Recycling Process of \textit{o-Benzenedisulfonimide}}

After separating polymers from cold methanol, the residue solution was evaporated under vacuum followed by an addition of Et$_2$O and H$_2$O (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 $^1$H NMR spectrum of $o$-benzenedisulfonimide.
Fig. S3. $^{13}$C NMR spectrum of o-benzenedisulfonimide.
**Fig. S4** $^1$H NMR spectrum of PVL-$b$-PCL initiated from BnOH in CDCl$_3$.

**Fig. S5** $^1$H NMR spectrum of PCL-$b$-PVL initiated from BnOH in CDCl$_3$.

**Fig. S6** SEC traces of the resulting PVL initiated by H$_2$O.
Fig. S7 ¹H NMR spectrum of PCL initiated from H₂O in CDCl₃.

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  $^{13}$C 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.