Supporting Information

Ultrafast and Selective Recycling Poly(p-dioxanone) to Monomers by Using Brønsted-Lewis Acidic Ionic Liquids as Solvent/Catalyst

Experimental Section

1. Materials

Zinc chloride (ZnCl₂, A.R.), Copper chloride (CuCl₂, A.R.), Pentaerythritol (PER, A.R.) were obtained from KHRON CHEMICALS (Chengdu, China). Ferric chloride (FeCl₃, A.R.) was obtained from Shanghai Shanpu Chemical Co., Ltd (Shanghai, China), Triethylamine (Et₃N, A.R.), p-Toluenesulfonic acid (TsOH, A.R.) were obtained from Fuchen (Tianjin) Chemical Reagent Co., Ltd. (Tianjin, China). Triethylamine hydrochloride ([Et₃NH]Cl, A.R.), Methanesulfonic acid (MeSO₃H, A.R.), Stannous octoate (SnOct₂, RG) were obtained from Adamas-beta[®]. PDO was obtained from the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China).

2. Instruments

Thermogravimetric Analysis (TGA) curves were measured the by thermogravimetric analyzer in an atmosphere of N₂ with a flow rate of 25 mL min⁻¹ over a temperature range from room temperature to 600 °C at a heating rate of 10 °C min⁻¹. The mass spectrum was measured by SCIEX X500R Quadruple Ultrahigh Resolution Time-of-Flight mass instrument (Q-TOF MS). Matrix-Assisted Laser Desorption/Ionization Time-of-flight Mass Spectra (MALDI-TOF MS) were recorded on a Bruker Autoflex III spectrometer (reflect model), with 355 nm laser and 20 KV voltage ion source. PPDO samples were dissolved in CHCl₃ at a concentration of 2 mg·mL⁻¹, and then mixed with the matrix α -Cyano-4hydroxycinnamic acid (CHCA). Intrinsic viscosity i.e. $[\eta]$ was measured at 30 °C with a concentration of about 0.1 g·dL⁻ ¹ in phenol/1,1,2,2-tetrachloroethane (1/1, volume ratio) solution using an Ubbelohde viscometer. The Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrophotometer scanning from 4000 cm⁻¹ to 500 cm⁻¹. Nuclear Magnetic Resonance (NMR) spectra of the samples were recorded on a Bruker Avance III spectrometer operating at 400 MHz in dimethyl sulfoxide (DMSO-d6) or CDCl₃. Gas Chromatography (GC) was performed on an Agilent 7890B system equipped with HP-5 capillary column. Samples were injected (0.4 μ L) in split mode (20:1), with the injector temperature at 250°C. The column temperature was programmed in a range of 80°C (5 min) – 20°C·min⁻¹ – 200°C (5 min). The FID detector temperature was 280°C.

3. Preparation of AILs

AILs were synthesized from previous literature.^{1, 2} Equimolar amounts of Et₃N (0.2 mol, 20.24 g) were slowly added to TsOH (0.2 mol, 34.44 g)/MeSO₃H (0.2 mol, 19.22 g) at 60°C for 4 h until a homogeneous solution was obtained. Et₃NHCl (0.1 mol, 13.77 g) was mixed with ZnCl₂ (0.1 mol, 13.63 g), CuCl₂ (0.1 mol, 13.45 g), and FeCl₃ (0.1 mol, 16.22 g) respectively and heated to 80°C under stirring until a clear liquid was obtained. Then the AILs were dried in a vacuum oven at 80°C for 12 h.

4. Polymerization and Depolymerization of PPDO

PDO was dried over CaH₂ for 6 h, followed by reduced pressure distillation. In a three-mouth flask, PDO (1 mol, 102.10 g) was added first, 1 mol% H₂O (10 mmol, 0.18 mL) as initiator, and 0.01 mol% SnOct₂ (0.1 mmol, 40 mg) as catalyst were added separately, and the reaction was carried out at 80°C for 6 h under N₂ atmosphere. Then, the product was purified by precipitation from the hexafluoroisopropanol solution in methanol and dried under vacuum to a constant weight. The viscosity-average molecular weight is 1.4×10^4 Da according to the inherent viscosity measurement ([η] = 0.32 dL·g⁻¹). Higher molecular weight PPDO sample (PPDO*, [η]=1.43 dL·g⁻¹, M_n=1.5×10⁵ Da) was obtained using the same method without loading extra initiator.

The PPDO depolymerization device was reported in our previous literature.¹ Specifically, a reaction flask with a cooling device and a collection device connected to a vacuum line. Typically, 5.22 g [Et₃NH][ZnCl₃] was added into the reaction flask firstly, and dried in vacuum line at 80°C for 4 h. Then, 2.58g PPDO (m_0) was added under the N₂ atmosphere. Next, the depolymerization was conducted under 100±20 Pa at 140 °C, with stirring and oil bath heating. When no more substance was distilled, the reaction was stopped and the system was fed with an N₂ atmosphere. Afterward, the distilled PDO monomer (in a cooled collection device) was weighed (m_1), and the yield

was calculated according to the following formula and tested for purity using GC.

PDO yield = $m_1/m_0 \times 100\%$ (Eq1)

5. Apparent kinetics of the CRM of PPDO

The CRM of PPDO was controlled by the following kinetic Eq2:

$$dx/dt = k'$$
 (Eq2)

where k'=k[OH], k represents the rate constant for the conversion of PPDO, and [OH] represents the concentration of terminal hydroxyl groups, which is constant. x represents the PPDO conversion at a reaction time of t. The yield of distilled PDO is used in our system as the rate of PPDO conversion because the PDO generated from the reaction can be distilled in time. Thus, **Eq2** can be written as follows:

$$dy/dt = k'$$
 (Eq3)

where y represents the PDO yield at a reaction time of t. Integrating Eq3 against time yielded Eq4:

$$y = k' t$$
 (Eq4)

6. Methods and calculations for Economic and environmental evaluation

The Energy Economy factor (ε) mainly reflects the ability of the reaction to rapidly react at lower temperatures. The specific formula is as follows:

$$\varepsilon = Y / (T \times t)$$
 (Eq5)

where t is the reaction time (in minutes), T is the reaction temperature in degrees celsius, and Y is the yield of the main monomer in mass fraction.

Environmental factor (E) primarily serves to estimate the environmental impact of reagents used in the reaction.

$$E = mass of waste / mass of product$$
 (Eq6)

In the methanolysis of poly(cyclic esters), considering that it has been established that 90% of solvents are recycled. *E* calculated by the following equations:

$$E = \frac{\left[0.1 \times \left(\frac{solvent/alcohols}{polymer} ratio\right) + \left(\frac{cat}{polymer} ratio\right)\right] \times m_{polymer}}{yield_{product} \times \frac{MM_{product}}{MM_{polymer}} \times m_{polymer}}$$
(Eq7)

However, when IL is used as solvent/catalyst, it can be directly next depolymerized with easy recycling and only a small fraction (1%) of it is wasted. E is calculated by the following equations:

$$E = \frac{\left[0.01 \times \left(\frac{solvent/cat}{polymer} ratio\right)\right] \times m_{polymer}}{yield_{product} \times \frac{MM_{product}}{MM_{polymer}} \times m_{polymer}}$$
(Eq8)

Environmental Energy impact factor (ξ) is the integrated assessment of depolymerization efficiency and impact on the environment. ξ is calculated by the following equations:

$$\xi = E / \varepsilon \qquad (Eq9)$$

where E is the Environmental factor, and ε is the Energy Economy factor.

Supplementary Data



Fig. S1 ¹H NMR (DMSO-d6) spectra of reacting mixtures with adding PER.



Fig. S2 GC purity of PDO samples recycled at different reaction temperatures.



Fig. S3 ¹H NMR (DMSO-d6) spectra of PPDO/[Et₃NH]TsO mixtures with different mol ratios and its partly enlarged views.

Reaction temperature/°C	Regressive equation	Linear correlative coefficient
120	y=0.0177x	0.9993
130	y=0.0284x	0.9959
140	y=0.0442x	0.9994
150	y=0.0747x	0.9960
160	y=0.1078x	0.9982

Table S1 Linear regression results of the data in Fig. 5A

Table S2 Linear regression results of the data in Fig. 5B

Reaction temperature/°C	Regressive equation	Linear correlative coefficient
120	y=0.0221x	0.9983
130	y=0.0335x	0.9988
140	y=0.0537x	0.9971
150	y=0.0883x	0.9982
160	y=0.1345x	0.9959

References

1. F. T. Li, Y. Liu, Z. M. Sun, L. J. Chen, D. S. Zhao, R. H. Liu and C. G. Kou, *Energy Fuels*, 2010, **24**, 4285–4289.

2. G. Q. Tian, Z. H. Yang, W. Zhang, S. C. Chen, L. Chen, G. Wu and Y. Z. Wang, *Green Chem.*, 2022, **24**, 4490–4497.