

Chromophore initiator as a tool for exploring ring-opening polymerization of cyclic oxalates

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Experimental Section

1. Materials

Propylene glycol (Pg, Sigma-Aldrich, USA) was dried over molecular sieves 4Å and vacuum distilled. Tetrahydrofuran (THF) (Component-Reaktiv, Russia) was distilled over KOH, refluxed over sodium metal with benzophenone (Sigma-Aldrich), and distilled on the day of the experiment. Pyridine (Component-Reaktiv, Russia) was dried by heating over NaH under reflux and further distillation. Oxalyl chloride, 1-pyrenebutanol (Pyr-OH, Sigma-Aldrich, USA), tin(II) octanoate (Sn(Oct)₂, ABCR, Germany), and CDCl₃ (CarlRoth, Germany) were used as received without purification.

2. Synthesis of Cyclic PrOx

PrOx was synthesized as previously reported.^{S1} The resulting monomer was stored under argon in a desiccator over dry NaOH at 4 °C and was handled in the stream of argon. ¹H NMR (CDCl₃, 600 MHz, Figure S1) δ : 1.49 (d, ³J 6.6 Hz, 3H, Me), 4.46 (dd, ²J 12.7, ³J 9.0 Hz, 1H, CH₂), 4.53 (dd, ²J 12.7 Hz, ³J 2.6 Hz, 1H, CH₂), 4.99 (dq, ³J 9.0 Hz, ³J 6.6 Hz, ³J 2.6 Hz, 1H, CH).

3. Polymerization of the PrOx

The ring-opening polymerization of propylene oxalate was carried out in the bulk at 100 °C. An aliquot of monomer (0.1 g, 0.77 mmol) was placed into a flame-dried ampule filled with argon. The ampule was connected to the vacuum line and underwent three pumping and argon filling cycles at 50 °C. The solution of Sn(Oct)₂ (0.1 M) containing the appropriate amounts of initiator (1-pyrenebutanol) in dry THF (50 μ L) was introduced into the ampule using a gas-tight syringe (Hamilton Company, USA). The mixed sample was frozen using liquid nitrogen. Then the solvent was removed under vacuum. The ampule was sealed up under reduced pressure and stored at -20 °C. The samples were polymerized by immersing the ampoules in an oil bath maintained at 100 °C for a predefined time interval.

4. Size exclusion chromatography (SEC)

Size-exclusion chromatography of the obtained polymers was performed in THF at 40 °C with a flow rate of 1 mL·min⁻¹. The chromatographic system consisted of Altex pump, Knauer Smartline RI detector, Waters UV detector, Rheodyne® 7125 Front-Loading Injector, and HR-3 and HR-4 Ultrastyrigel columns. The polystyrene standard samples (Waters, USA) were used to calibrate the system. UV detection was performed at 343 nm for the samples containing a pyrene moieties.

5. Nuclear Magnetic Resonance Spectrometry (NMR)

NMR experiments were conducted using Bruker Avance 600 spectrometer at 303 K. The samples for NMR analysis were dissolved in CDCl₃ (Chemical Line, Russia). The chemical shifts δ_H were measured in ppm with respect to the residual protic solvent (CHCl₃, δ_H = 7.27 ppm). Content of initiator in samples

was determined by integration of signals at 3.4 ppm (CH₂ in α position relative to aromatics of Pyr-OH, 2H). The oligomers content was determined by the integral intensity of the shoulder at 5.38 ppm. For this purpose, we deconvolved the signal within the 5.25-5.45 ppm region and calculated the ratio of integral intensities of signals with maxima at 5.33 (CH of the polymer repeat units) and 5.38 ppm (CH of the oligomers). The reliability of this assessment is determined by the high working frequency and therefore the resolution capacity of the spectrometer used.

Signals of end-groups (5.12 ppm for primary hydroxyl, 4.13 ppm for secondary hydroxyl, and 3.4 ppm for pyrene moieties) were used to calculate number-average polymerization degree using the Equation S1.

$$P_n(NMR) = \frac{2 \cdot C(PrOx) \cdot \omega}{C(e.g.)} \quad (S1)$$

where $C(PrOx)$ – the concentration of PrOx consumed during polymerization, $C(e.g.)$ – total concentration of end groups, ω – the fraction of ROP linear products determined as described elsewhere. The coefficient 2 reflects two end groups in PPOx.

6. UV and Fluorescence spectroscopy

UV-spectra of PPOx samples and neat 1-pyrenebutanol dissolved in THF (0.4 mg·mL⁻¹) were recorded using an UtrospecPRO spectrophotometer (GE Healthcare) in 1 cm quartz cell (220–600 nm). Fluorescence spectra of THF solutions of PPOx samples (0.4 mg·mL⁻¹) were recorded using a Hitachi 650-10S spectrofluorimeter (Hitachi, Japan) in 1 cm quartz cell.

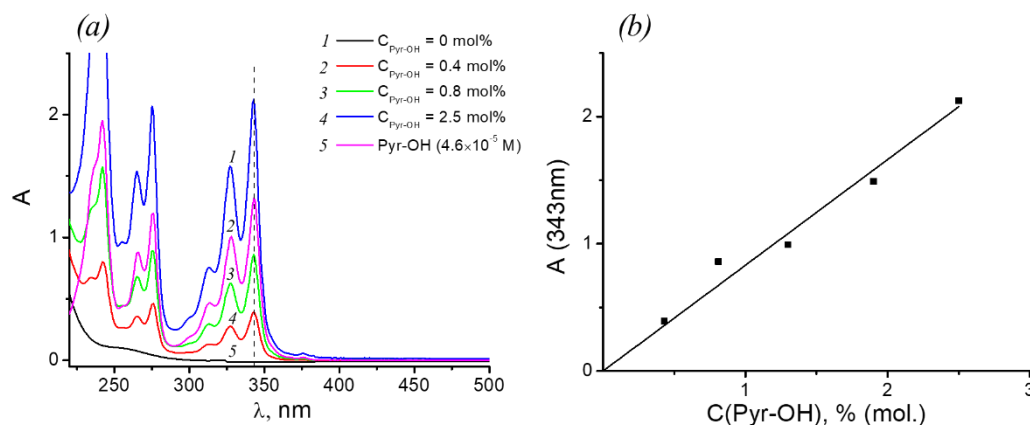


Figure S1. (a) Absorbance spectra of 0.04 mas% solutions of poly(propylene oxalate) samples in THF polymerized in the absence of Pyr-OH (1), and in the presence of 0.43 mol% (2), 0.81 mol% (3), and 2.47 mol% (4) of Pyr-OH. Curve 5 corresponds to 4.6×10⁻⁵ mol·L⁻¹ solution of Pyr-OH in THF. Dotted line shows the wavelength of maximum absorbance used in the work for detection of Pyr-PPOx in SEC eluate using UV-detector. (b) The dependence of absorbance at 343 nm of 0.04 mas% solutions of poly(propylene oxalate) samples on the content of Pyr-OH in the polymerization mixture.

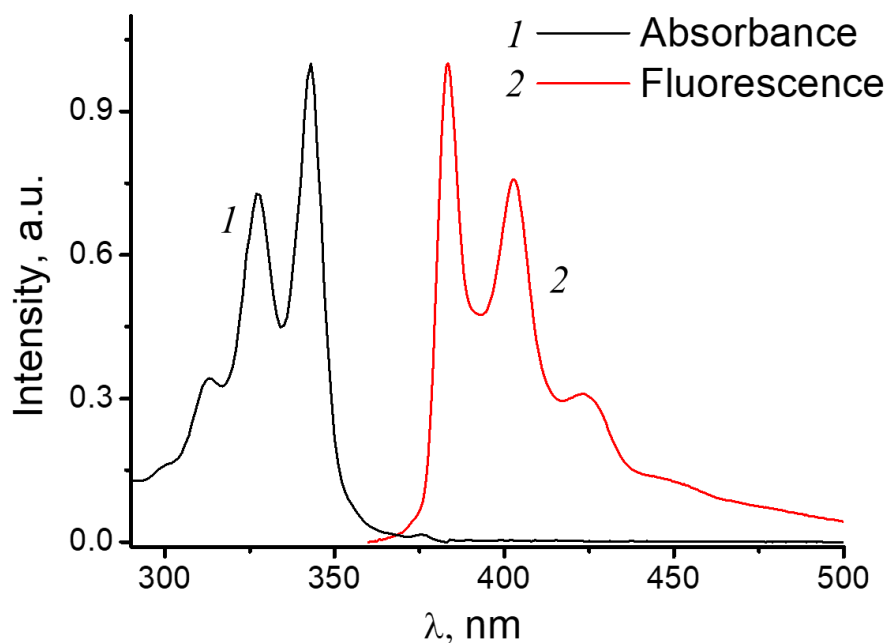


Figure S2. Normalized absorbance (curve 1), and fluorescence (curve 2) spectra of PPOx synthesized using Pyr-OH as initiator at $C(\text{Pyr-OH}) = 0.81 \text{ mol\%}$. The sample was dissolved in THF ($0.4 \text{ mg}\cdot\text{cm}^{-3}$).

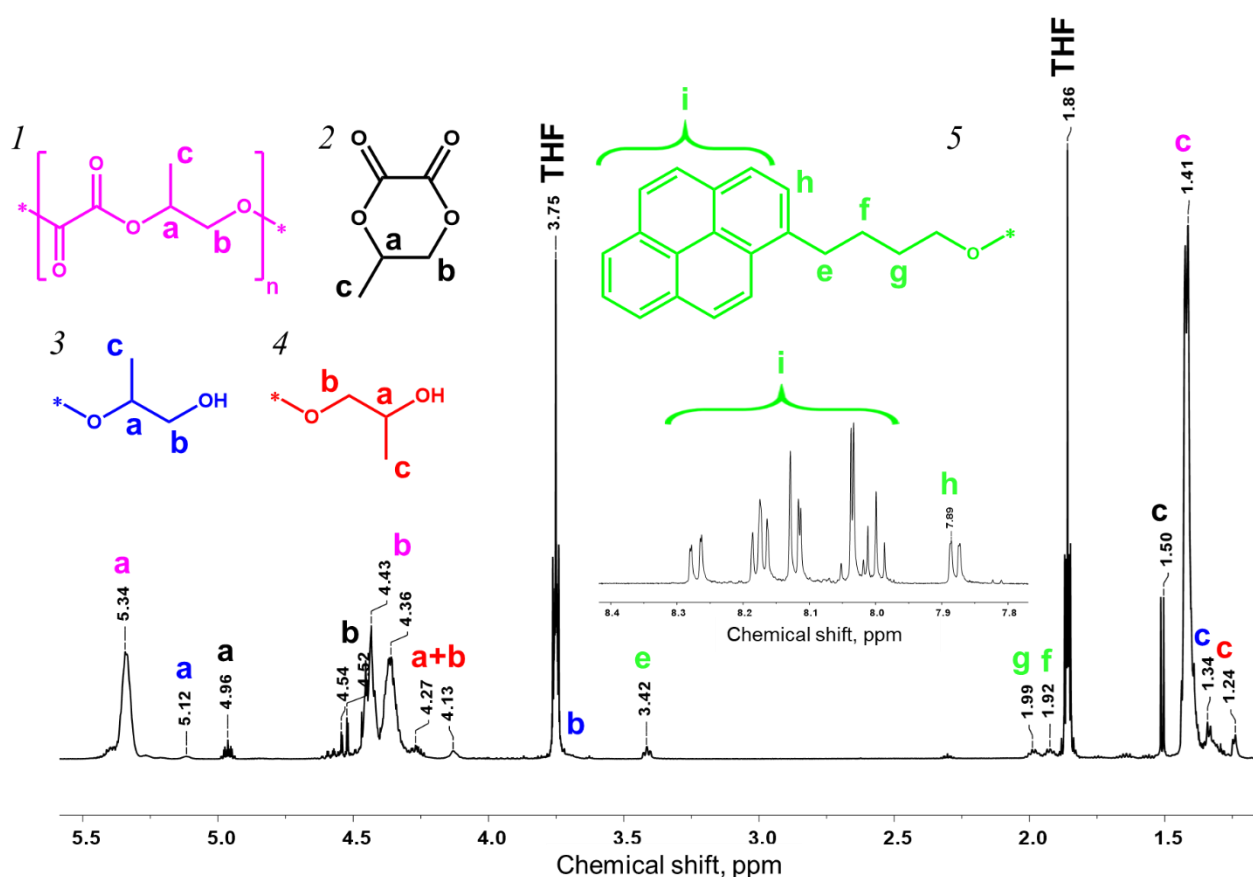


Figure S3. ^1H NMR spectrum of PPOx initiated with Pyr-OH at $C(\text{Sn}(\text{Oct})_2) = 0.65 \text{ mol\%}$, $C(\text{Pyr-OH}) = 2.47 \text{ mol\%}$, 24 h 100 °C. Methine protons are marked by (a) letters, methylene – by (b) letters, methyl – by (c) letters. The signals of propylene glycol residues located inside the chain are labeled with magenta letters, those of the monomer – by black letters, those of the residues with primary OH-groups – by blue letters, and those with secondary OH-groups – by red letters. The inset depicts the signals of pyrene end groups and their assignments in green.

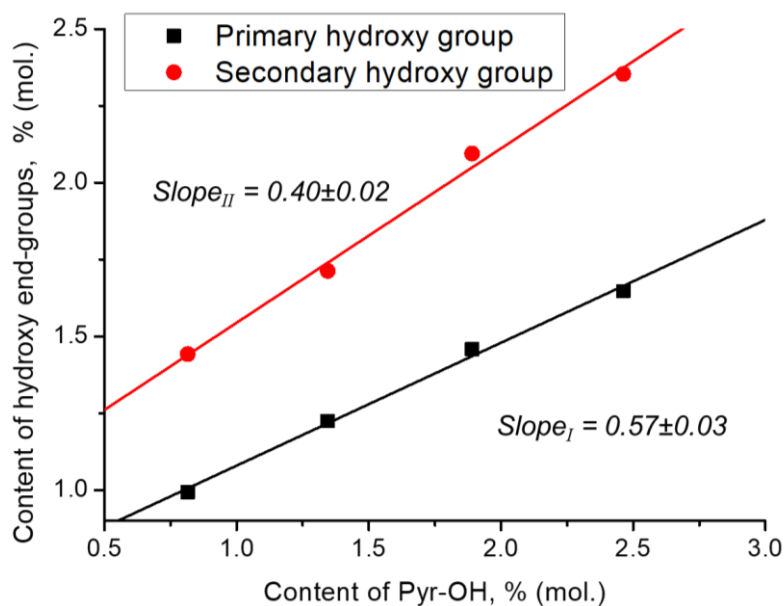


Figure S4. Linear dependences of the concentration of primary (squares) and secondary (circles) hydroxyl end-groups in linear PPOx on the concentration of Pyr-OH at 0.2 mol% of Sn(Oct)₂ at 100 °C at limiting degree of conversion (24 h).

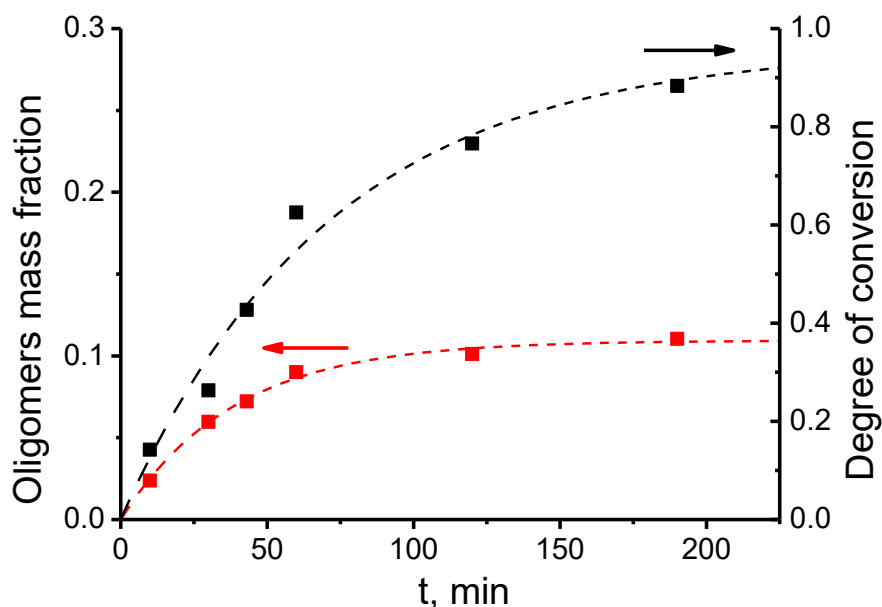


Figure S5. Kinetics of accumulation of oligomers (red points, left ordinate axis) and evolution of total conversion taking account of the sum of amounts of linear polymer and the oligomers (black points, right ordinate axis) at 0.2 mol% of Sn(Oct)₂, 0.5 mol% of Pyr-OH at 100 °C.

References

S1 N. P. Iakimov, E. M. Budynina, A. K. Berkovich, M. V. Serebryakova, V. B. Platonov, E. O. Fomin, A. G. Buyanovskaya, I. V. Mikhhev and N. S. Melik-Nubarov, *Eur. Polym. J.*, 2024, **220**, 113410; <https://doi.org/10.1016/j.eurpolymj.2024.113410>.