Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Borane Lewis Pair-Mediated Ring-Opening Polymerization of Epoxides: Direct Access to α-Acyl Azide/ω-Hydroxyl Heterotelechelic Polyethers and Latent Isocyanate Derived Polyurethane

Xianhao Xin[a], Wenyan Wang[a], Hua-an Wang[a], Wu Gao[b,*], Xinhui Kou[c,*], Chuanli Ren[d,*], Xiaowu Wang[a,e,*]

[a] *College of Chemical Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao, 266042, China. E-mail: wangxw@qust.edu.cn*

[b] *Kaili Catalyst New Materials CO., LTD, Xi'an Economic and Technological Development Zone, 4288 Shanglin Road, Xi'an, 710018, China. E-mail: wu.gao@xakaili.com*

[c] *Analyses and Testing Center, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao, 266042, China. E-mail: kouxinhui@qust.edu.cn*

[d] *State Key Laboratory of Advanced Optical Polymer and Manufacturing Technology, College of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao, Shandong 266042, China. E-mail: chuanli@iccas.ac.cn*

[e] *State Key Laboratory of Advanced Optical Polymer and Manufacturing Technology, College of Chemical Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao, 266042, China. E-mail: wangxw@qust.edu.cn*

TABLE OF CONTENTS

Chemicals

Unless otherwise stated, all chemicals are used without further purification. Propylene oxide (PO) was purchased from Energy Chemical Co., 1-tert-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ⁵,4λ⁵-catenadi(phosphazene) , 4-fluorophenyl isocyanate , methanol , benzoic acid , Calcium hydride(CaH_2) and deuterated solvents were purchased from Macklin Co., Ltd. Tetrahydrofuran (THF) was purchased as Super-dry solvent from Energy Chemical Co., Ltd. 4-Hydroxymethylbenzoyl azide was synthesized from the corresponding carboxylic acid precursor by DPPA-mediated azidation according to literature procedures. **POSS** was synthesized according to the method previously published by our group. $CDCl_3$ and PO were dried over CaH_2 for 48 h, distilled and stored under nitrogen atmosphere.

Characterization and Analysis

NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (^{1}H NMR 400 MHz, ^{13}C{^{1}H} NMR 100 MHz, 128 MHz ^{11}B{^{1}H} NMR, 162 MHz ^{31}P NMR) at 298 K. ^{1}H and ^{13}C{^{1}H} NMR Chemical shifts were reported in δ (ppm) with the residual deuterated solvent peak as reference [^{1}H: TMS in $CDCl_3$ = 0 ppm; ^{13}C{^{1}H}: $CDCl_3$ = 77.16 ppm; ^{11}B{^{1}H}: BF_3*Et_2O (external standard) = 0 ppm, ^{31}P{^{1}H}: 85% H_3PO_4 (external standards) = 0 ppm]. Data are reported as follows: Chemical shift in ppm, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad signals, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation. The substitution pattern of phenyl group and assignments of phenyl carbon in ^{13}C{^{1}H} NMR were named as follows: ortho- (*o*-Ph), meta- (*m*-Ph), para- (*p*-Ph) and ipso- (*i*-Ph).

MALDI-TOF-MS

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating at a positive ion, linear mode (modified according to experiments). The polymer samples (10 mg mL^{-1}), trans-2[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 25 mg mL^{-1}) and CF_3COONa (5 mg mL^{-1}) were dissolved in THF and mixed in a volume ratio of 20:5:5 (Sample concentration, matrix type, ionic salt and volume ratio are modified according to experimental conditions). The weak higher-mass shoulders observed in some MALDI-TOF-MS spectra may originate from minor side species or different cationized adducts. Because MALDI ionization efficiency can vary significantly among polymer species, the relative intensities should not be directly interpreted as quantitative composition. Therefore, the MALDI data are used qualitatively to support the dominant end-group structure, in combination with NMR and FT-IR analyses.

GPC

Gel permeation chromatography (GPC) measurements of polymers PPO-0.5, PPO-1.0, PPO-1.5, PPO-2.0, PPO-10.0, and P2 were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector using THF as mobile phase at a flow rate of 1.0 mL min^{-1} at 40 °C. One PLgel 5 μm guard column and three Mz-Gel SDplus columns (10^3Å, 10^4Å and 10^5Å, linear range of $M_W = 1000 – 2*10^6$ Da) were connected in series. The molecular weight and dispersity were calculated using 6 polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for GPC analyses was 5-10 mg mL^{-1}.

Gel permeation chromatography (GPC) measurements of polymers P4-0.5, P4-1.0, P4-1.5, P4-2.0, and P4-10.0 were performed on a Waters 1515 HPLC system using DMF as the mobile phase at a flow rate of 1.0 mL min^{-1} and a detection wavelength of 263 nm. One PLgel 5 μm MIXED-C column (300 × 7.5 mm) was used for separation. The molecular weight and dispersity were calculated using six polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for GPC analyses was 5–10 mg mL^{-1}.

Differential Scanning Calorimetry (DSC)

Measurements were performed using a TA Instruments DSC 25. The temperature was calibrated using indium standards. The experiments were carried out under N_2 atmosphere at a heating rate of 10 °C/min over a temperature range of -80 to 60 °C, with a flow rate of 50 mL/min. The mass of each test sample was 5-10 mg.

Experimental procedure

General synthetic procedure for P1 polymers with different molecular weights

In a glovebox, propylene oxide (PO) (15 mmol, 1.05 mL, 3000 equiv.), POSS-B8 (5 μmol, 8 mg, 1 equiv.), and ^{t}BuP$_2$ (5 μmol, 2.5 μL, 1 equiv.) were added to a dry reaction vessel. Then, 4-hydroxymethylbenzoyl azide was added in an amount corresponding to the target molecular weight. The polymerization was conducted in bulk at 25 °C with a fixed feed ratio of [PO]/[**POSS-B8**]/[^{t}BuP$_2$] = 3000/1/1. After the desired reaction time, the polymerization was quenched with acetic acid, and an aliquot was taken for NMR analysis to determine the conversion, yielding α-acyl azide/ω-hydroxy-terminated poly(propylene oxide) (PPO) with the target molecular weight.

Synthetic Procedure for P2 and P3

In a glovebox, to a flame-dried 15 mL pressure vial equipped with a magnetic stir bar were added POSS-B8 (5 μmol, 8 mg, 1 equiv.), ^{t}BuP$_2$ (5 μmol, 2.5 μL, 1 equiv.), 4-(hydroxymethyl)benzoyl azide (0.955 mmol, 0.1692 g, 191 equiv.), and propylene oxide (PO) (15 mmol, 1.05 mL, 3000 equiv.) in sequence. The pressure vial was sealed and taken out of the glovebox. After polymerization at 25 °C for 2 h, α/ω-acyl azide/hydroxyl-terminated polyether with a target molecular weight of 1000 was obtained. Upon obtaining the α/ω-acyl azide/hydroxyl-terminated polyether with a target M_n of 1000, 4-fluorophenyl isocyanate (4.775 mmol, 543 μL, 955 equiv.) was added. The reaction was conducted at 25 °C for 20 h. After the reaction, excess 4-fluorophenyl isocyanate was removed using a vacuum pump to afford polymer **P2**. Subsequently, **P2** was heated in toluene solution at 110 °C for 2 h, which induced Curtius rearrangement of the acyl azide end groups, generating isocyanates in situ, to give the α,ω-isocyanate/urethane-terminated product **P3**.

Synthetic Procedure for P4

The successfully synthesized P1 polymers with different molecular weights were heated at 100 °C for 2 h to obtain P4 with corresponding molecular weights.

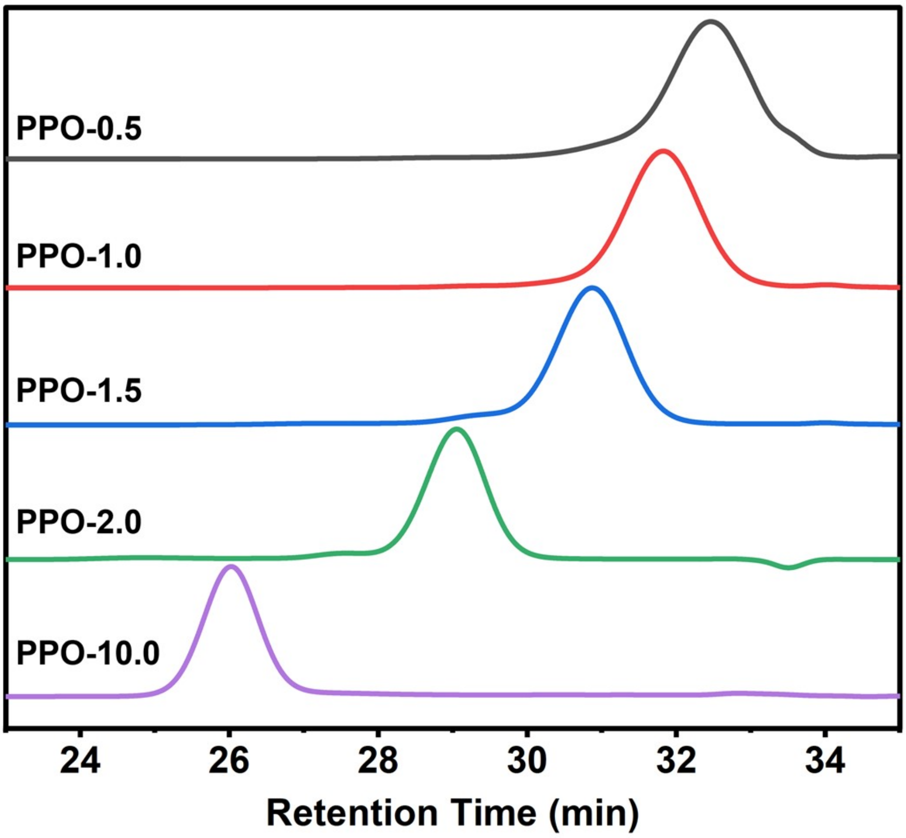

Fig. S1. GPC curves of the obtained α-acyl azide/ω-hydroxyl-terminated PPOs (Table 1, runs 1-5)

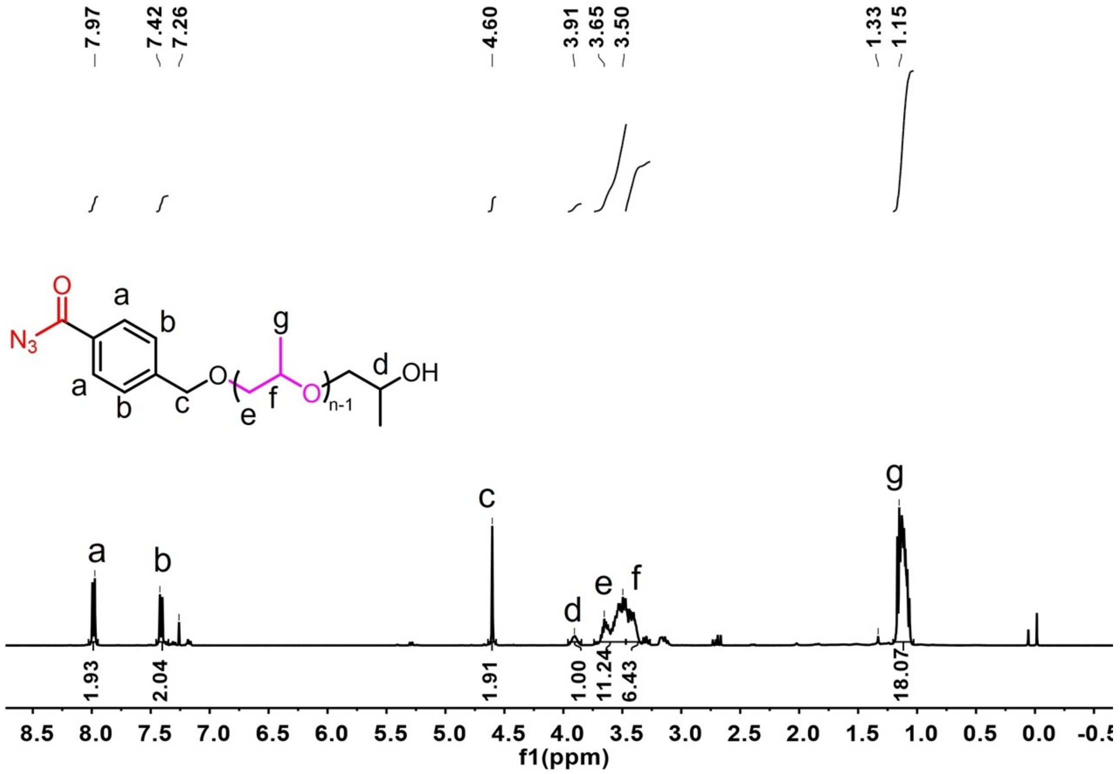

Fig. S2. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of obtained PPO from Table 1, run 1

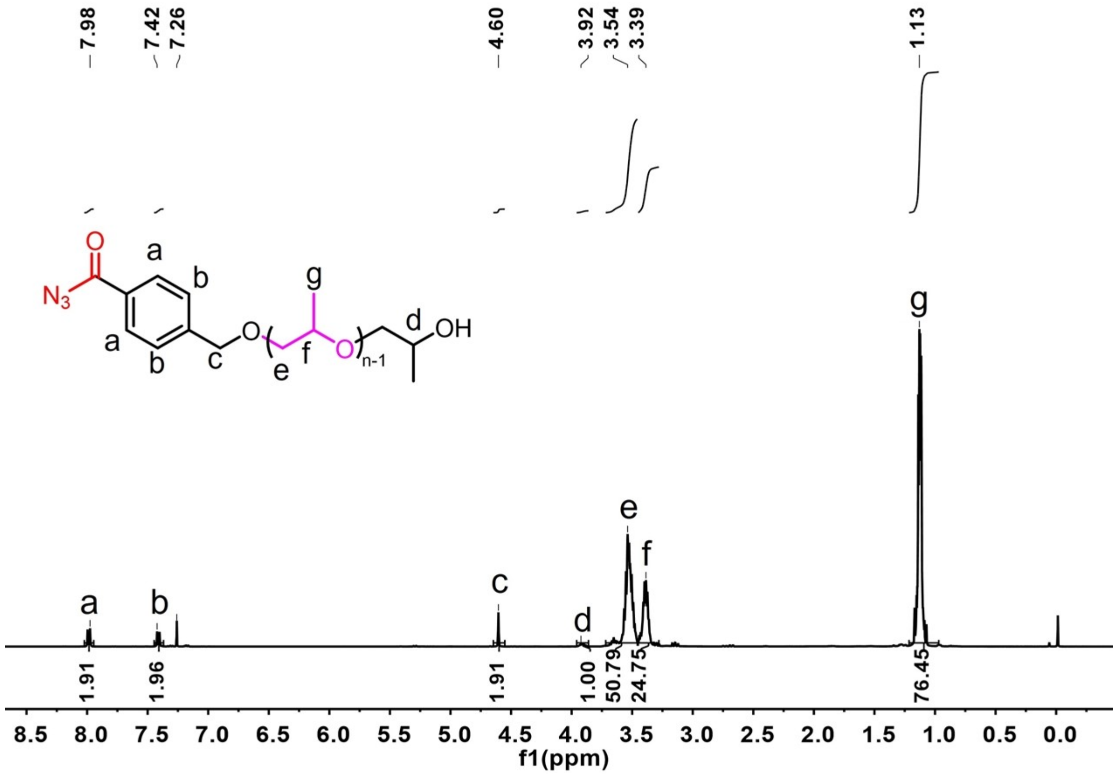

Fig. S3. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of obtained PPO from Table 1, run 3

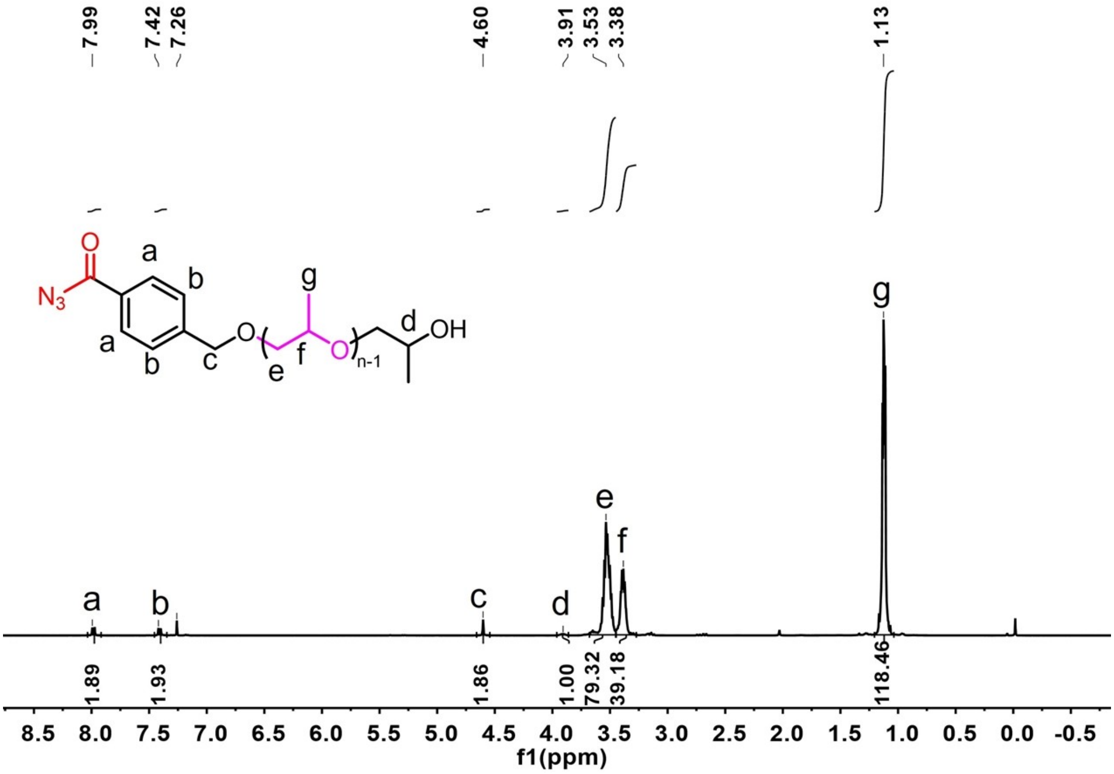

Fig. S4. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of obtained PPO from Table 1, run 4

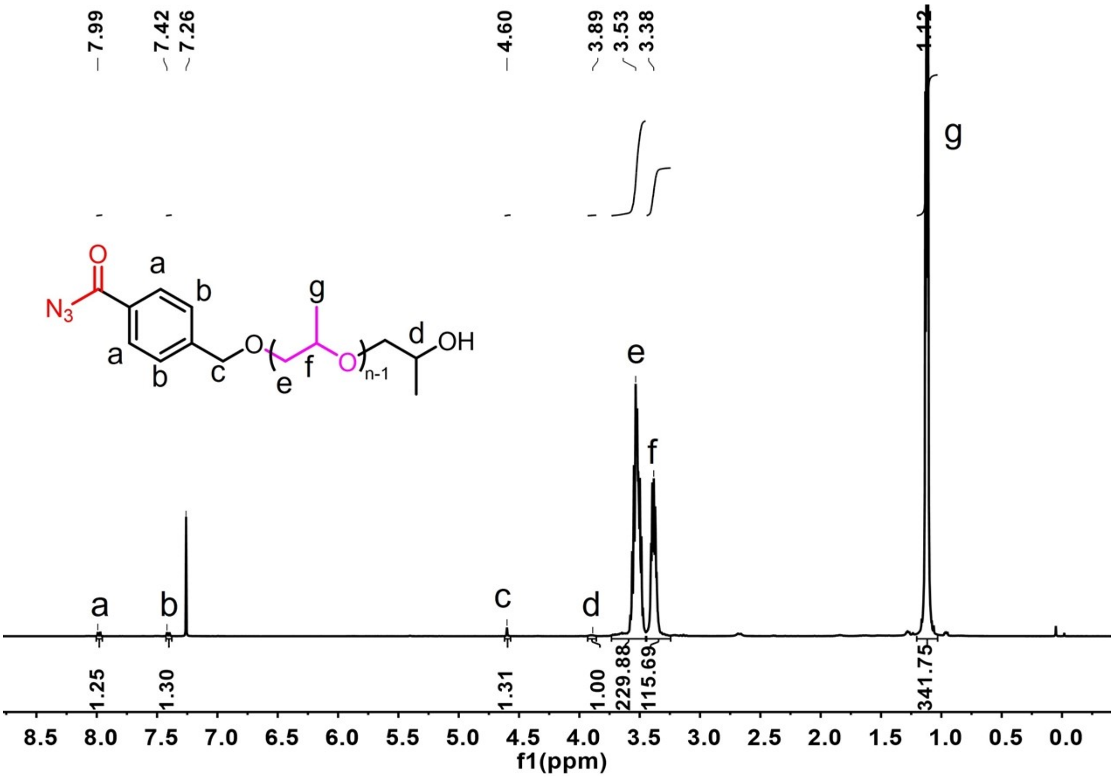

Fig. S5. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of obtained PPO from Table 1, run 5

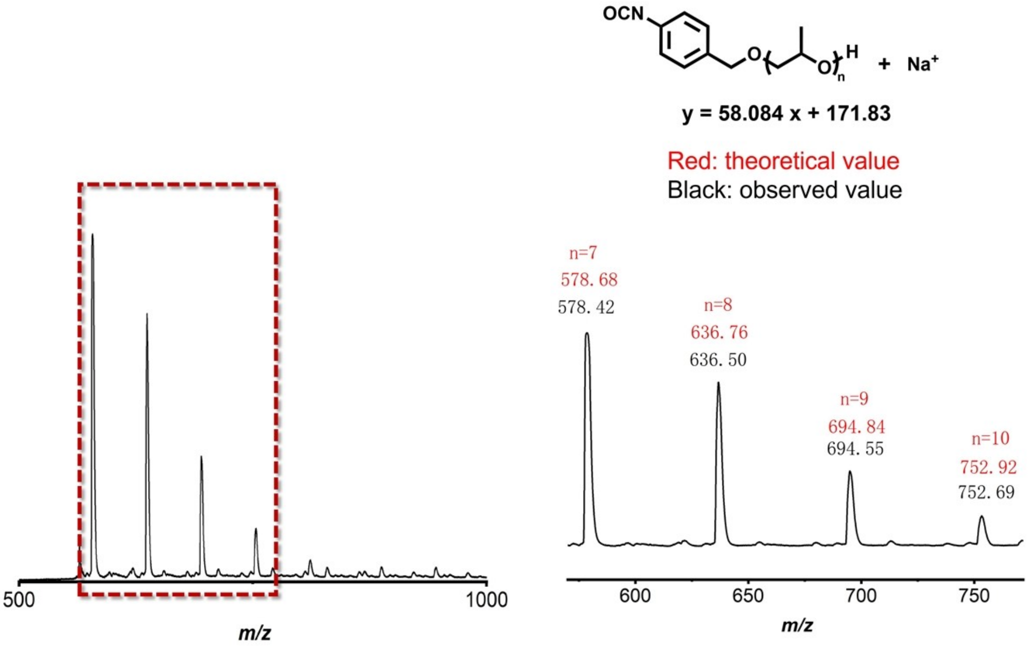

Fig. S6. MALDI-TOF-MS signals of PPO-0.5 measured with reflectron mode. The major peak series is assigned to α-4-isocyanatophenyl methanol/ω-hydroxyl PPO, with a repeating interval of 58 Da corresponding to the PO unit. The labeled values correspond to calculated m/z values for the assigned major series.

The weak higher-mass shoulders observed in some MALDI-TOF-MS spectra may originate from minor side species or different cationized adducts. Because MALDI ionization efficiency can vary significantly among polymer species, the relative intensities should not be directly interpreted as quantitative composition. Therefore, the MALDI data are used qualitatively to support the dominant end-group structure, in combination with NMR and FT-IR analyses. This interpretation is also applicable to the MALDI-TOF-MS spectra of the other PPO samples provided in the Supporting Information (Figs. S7–S9).

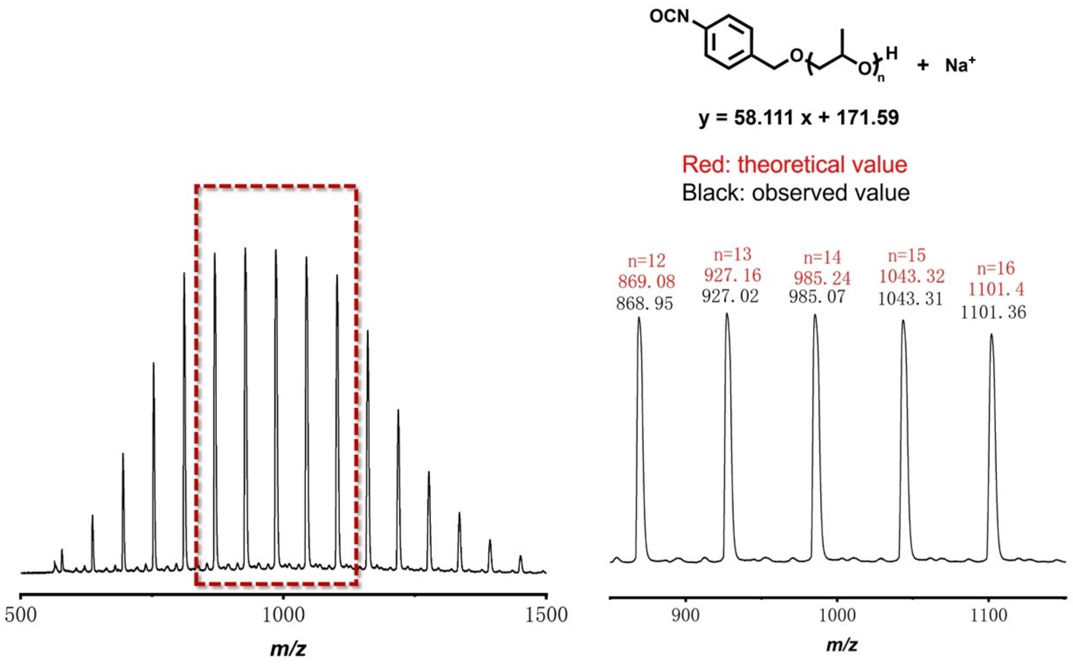

Fig. S7. MALDI-TOF-MS signals of PPO-1.0 measured with reflectron mode. The major peak series is assigned to α-4-isocyanatophenyl methanol/ω-hydroxyl PPO, with a repeating interval of 58 Da corresponding to the PO unit. The labeled values correspond to calculated m/z values for the assigned major series.

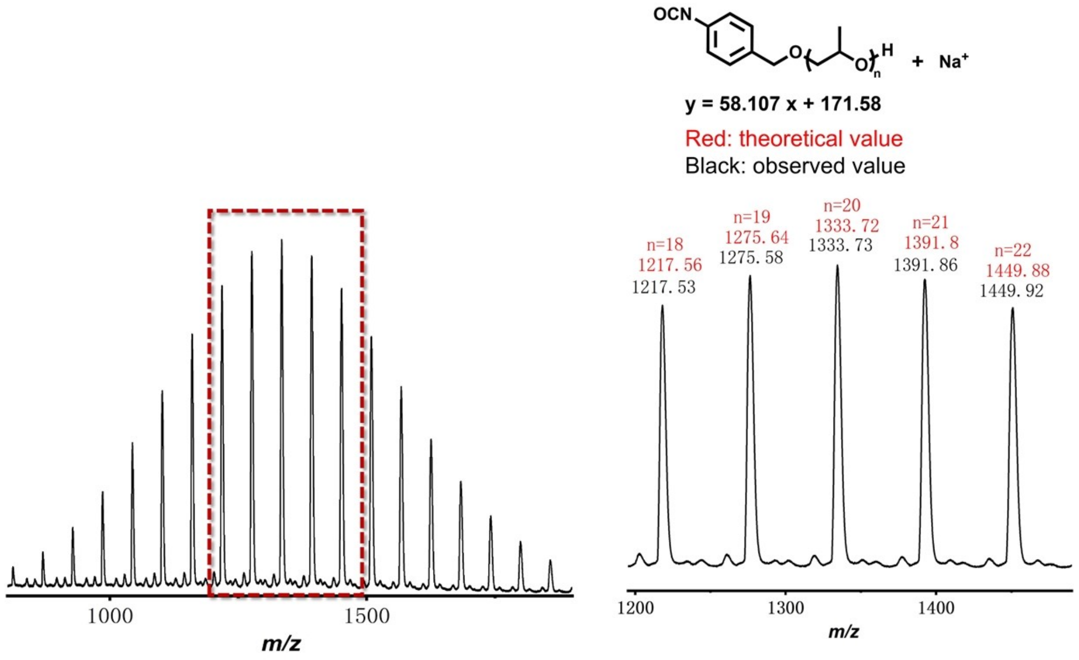

Fig. S8. MALDI-TOF-MS signals of PPO-1.5 measured with reflectron mode. The major peak series is assigned to α-4-isocyanatophenyl methanol/ω-hydroxyl PPO, with a repeating interval of 58 Da corresponding to the PO unit. The labeled values correspond to calculated m/z values for the assigned major series.

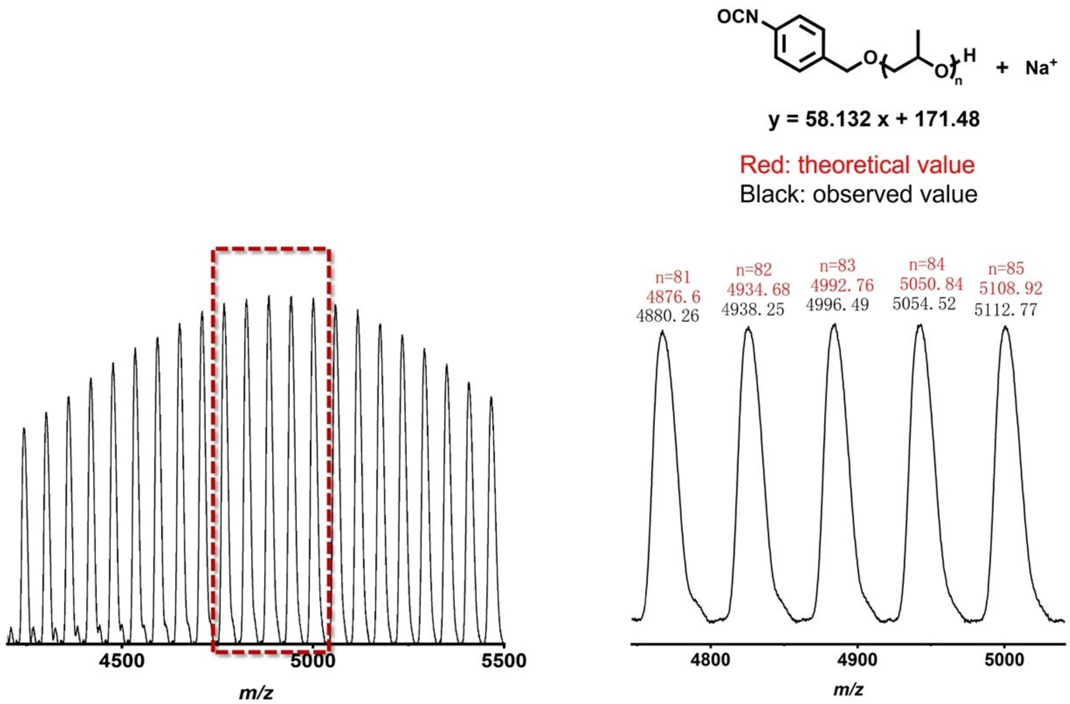

Fig. S9. MALDI-TOF-MS signals of PPO-10.0 measured with reflectron mode. The major peak series is assigned to α-4-isocyanatophenyl methanol/ω-hydroxyl PPO, with a repeating interval of 58 Da corresponding to the PO unit. The labeled values correspond to calculated m/z values for the assigned major series.

Table S1. Control experiments of ^{t}BuP$_2$/BEt$_3$ binary system for the ROP of PO in the presence of 4-hydroxymethylbenzoyl azide

Run	[PO]/[^{t}BuP$_2$]/[BEt$_3$]/[initiator]	Time (h)	Conversion(%)^a
1	3000/1/2/17	2	28.1
2	3000/1/8/17	2	94.5

The conversion was determined by ^{1}H NMR spectroscopy. 2 μmol ^{t}BuP$_2$ was used. The corresponding NMR spectra are shown in Fig. S10 and Fig. S11. It should be noted that when 1 equivalent of POSS-B8 was used as the Lewis acid, quantitative conversion of PO was achieved within 1.5 hours. In contrast, through our control experiments, even with 8 equivalents of BEt$_3$, the conversion reached only 94.5% after 2 hours.

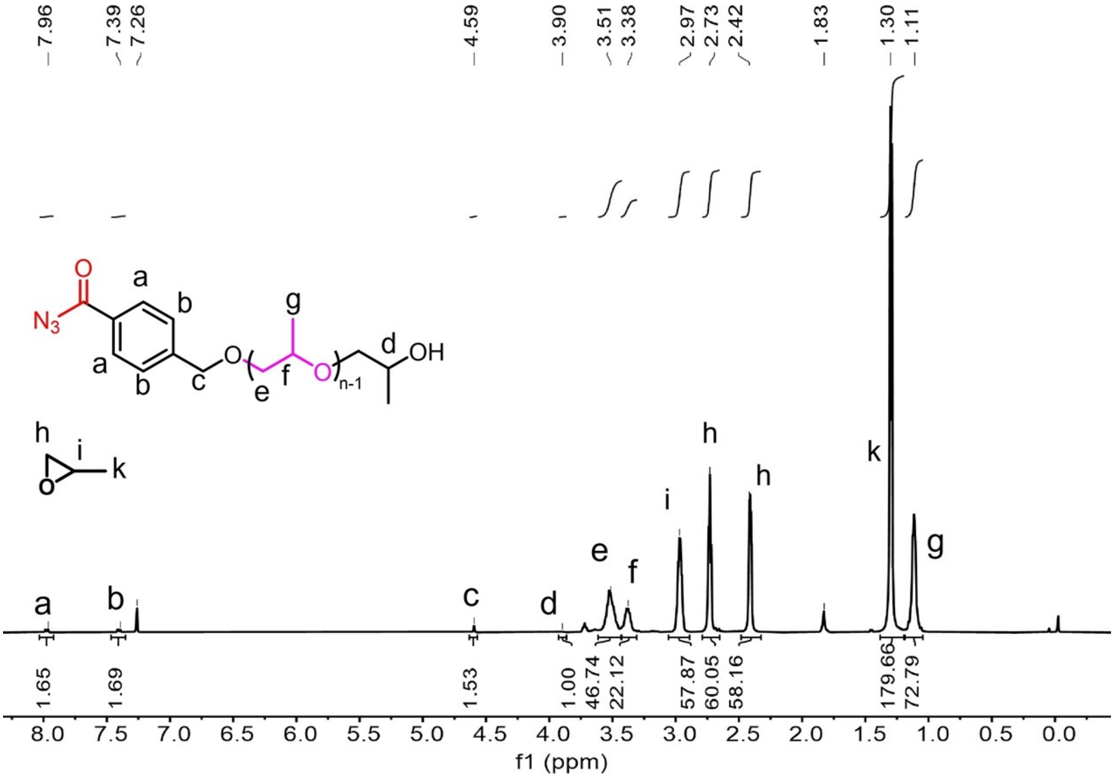

Fig. S10. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of Table S1, run 1.

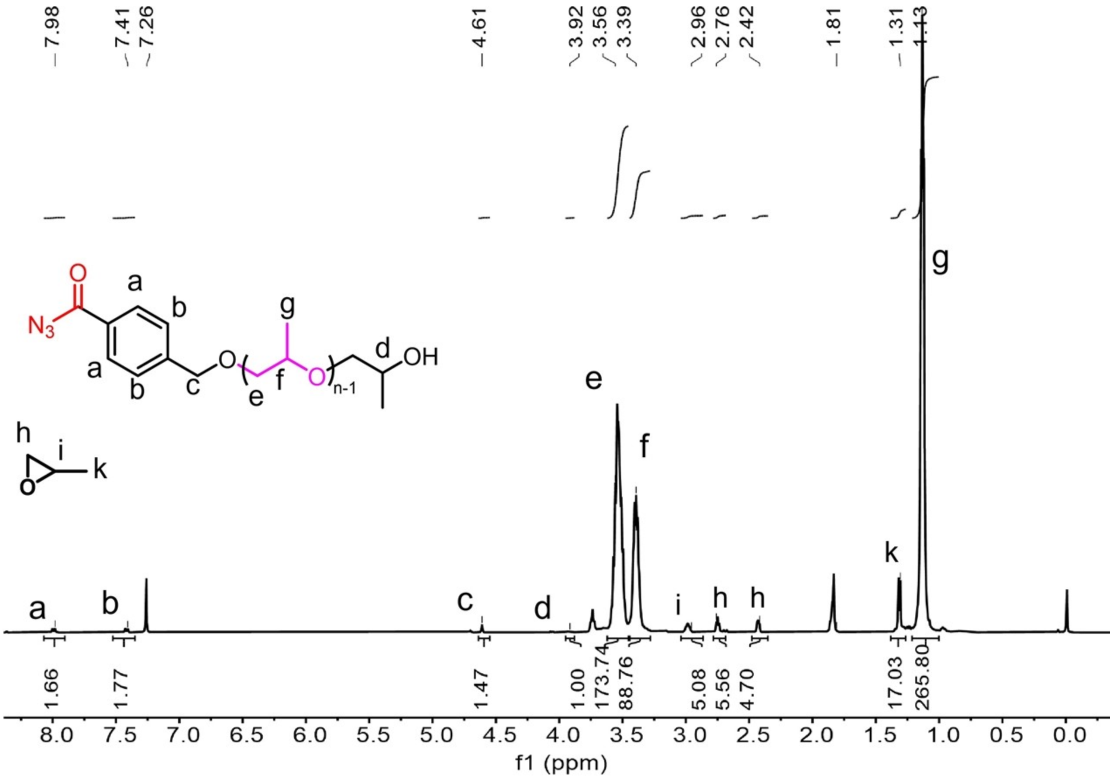

Fig. S11. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of Table S1, run 2.

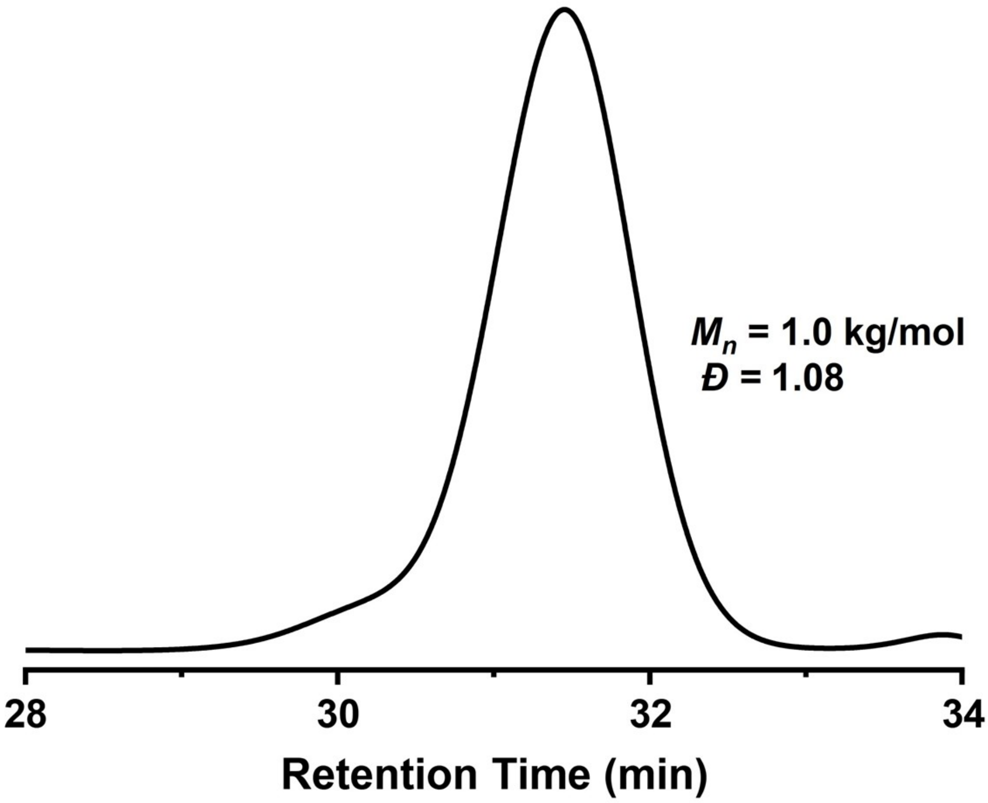

Fig. S12. GPC curve of P2-1.0

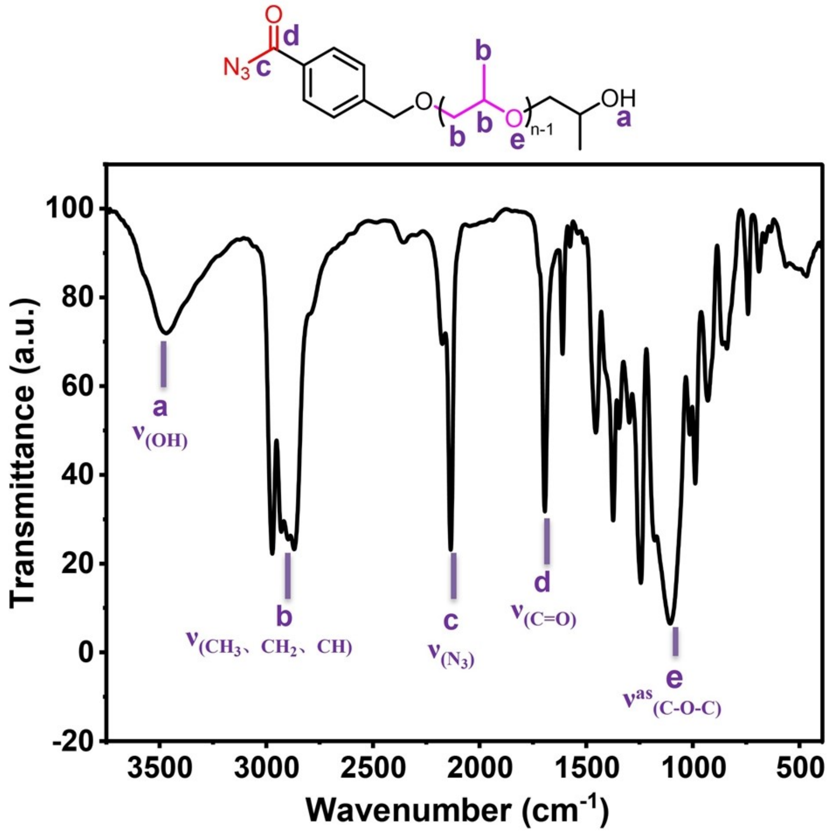

Fig. S13. FT-IR spectrum of PPO-1.0

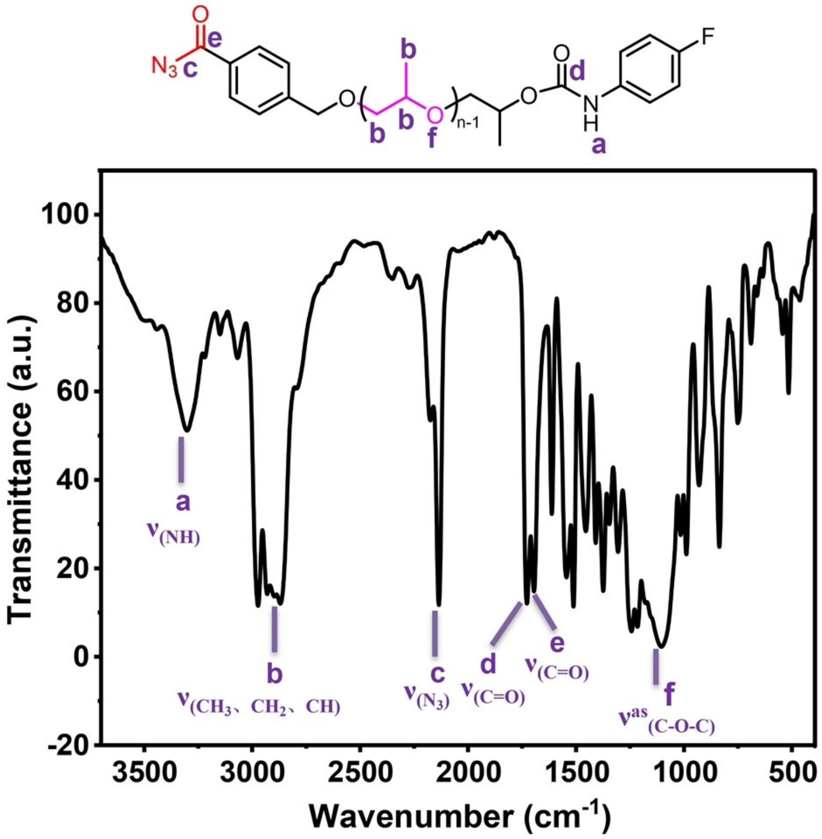

Fig. S14. FT-IR spectrum of α-benzoyl azide/ω-urethane PPO

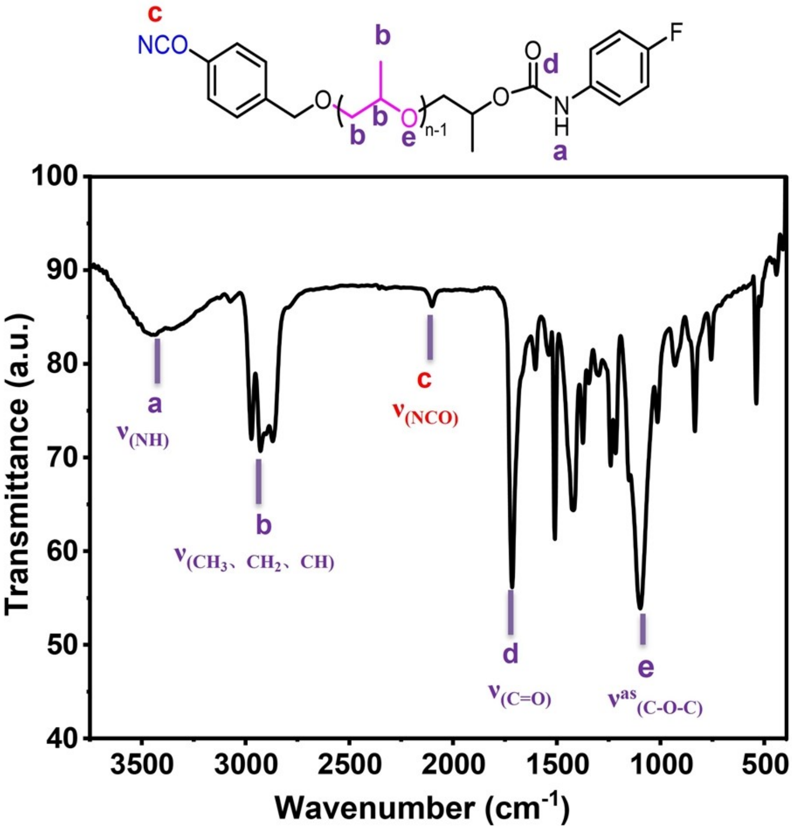

Fig. S15. FT-IR spectrum of **P3**

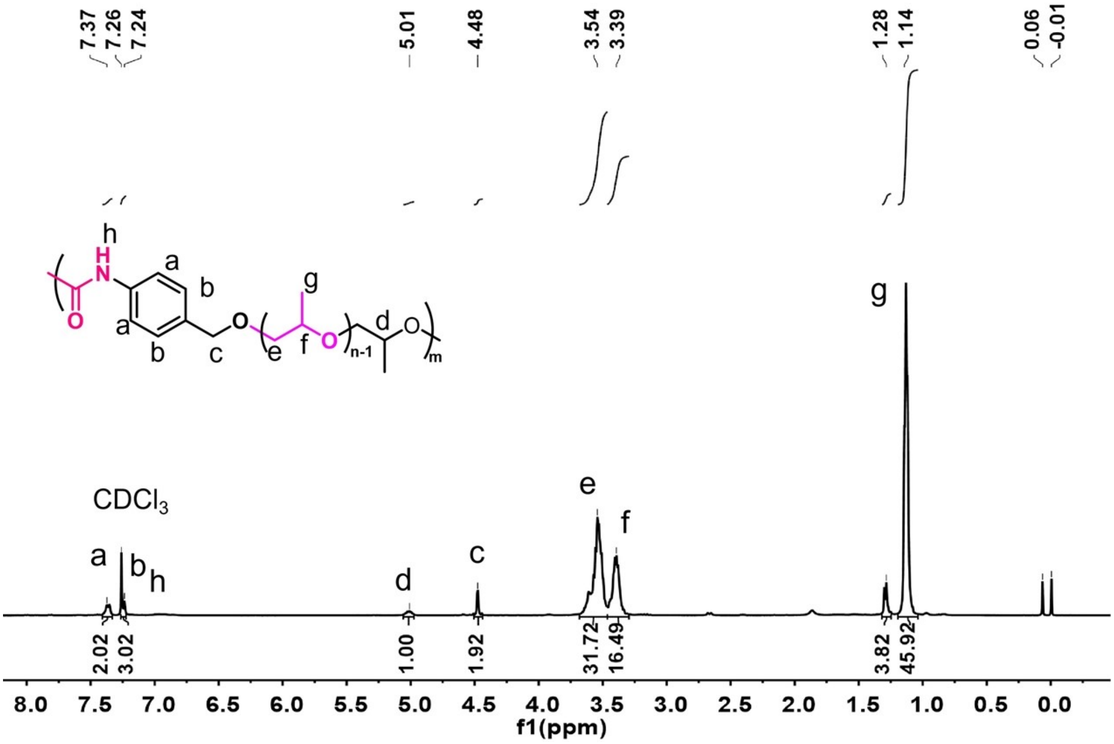

Fig. S16. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of obtained PPO from Table 2, run 2

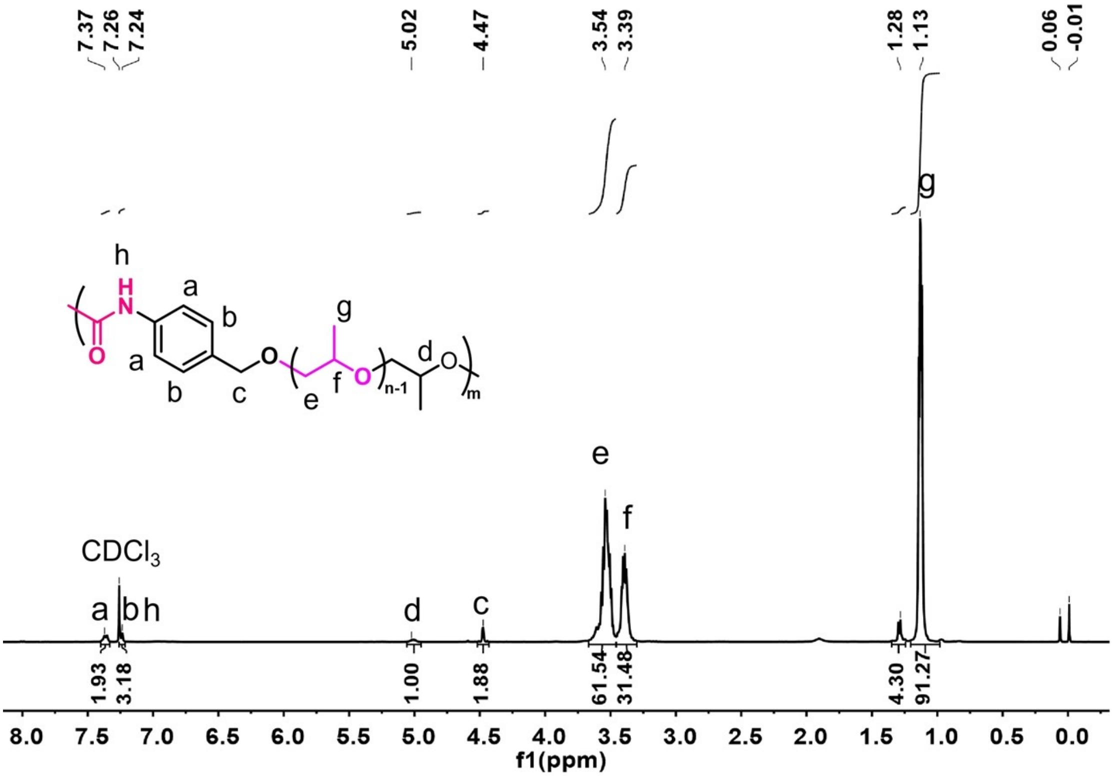

Fig. S17. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of obtained PPO from Table 2, run 3

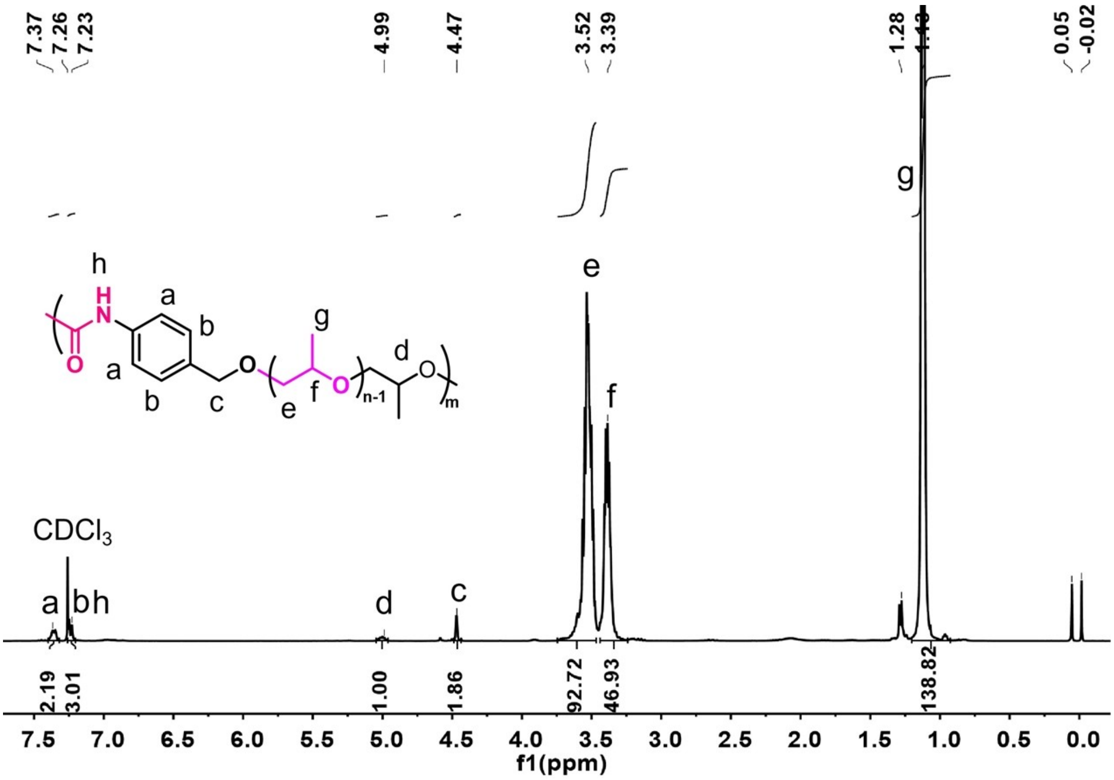

Fig. S18. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of obtained PPO from Table 2, run 4

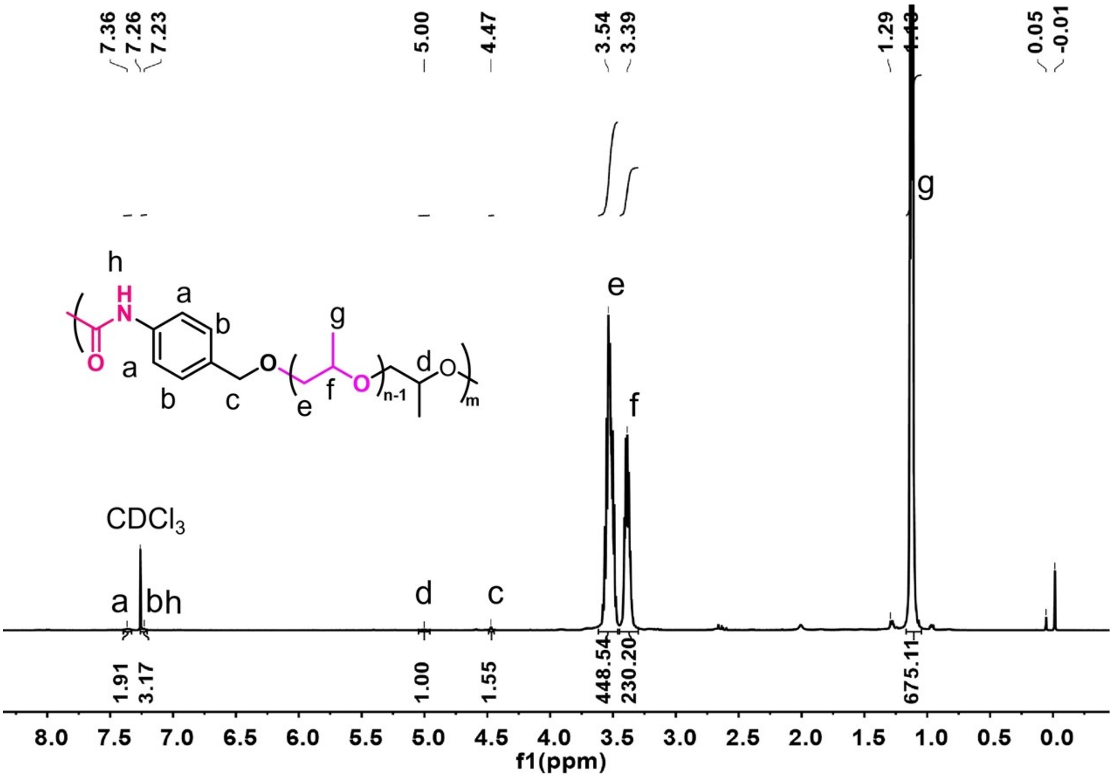

Fig. S19. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of obtained PPO from Table 2, run 5

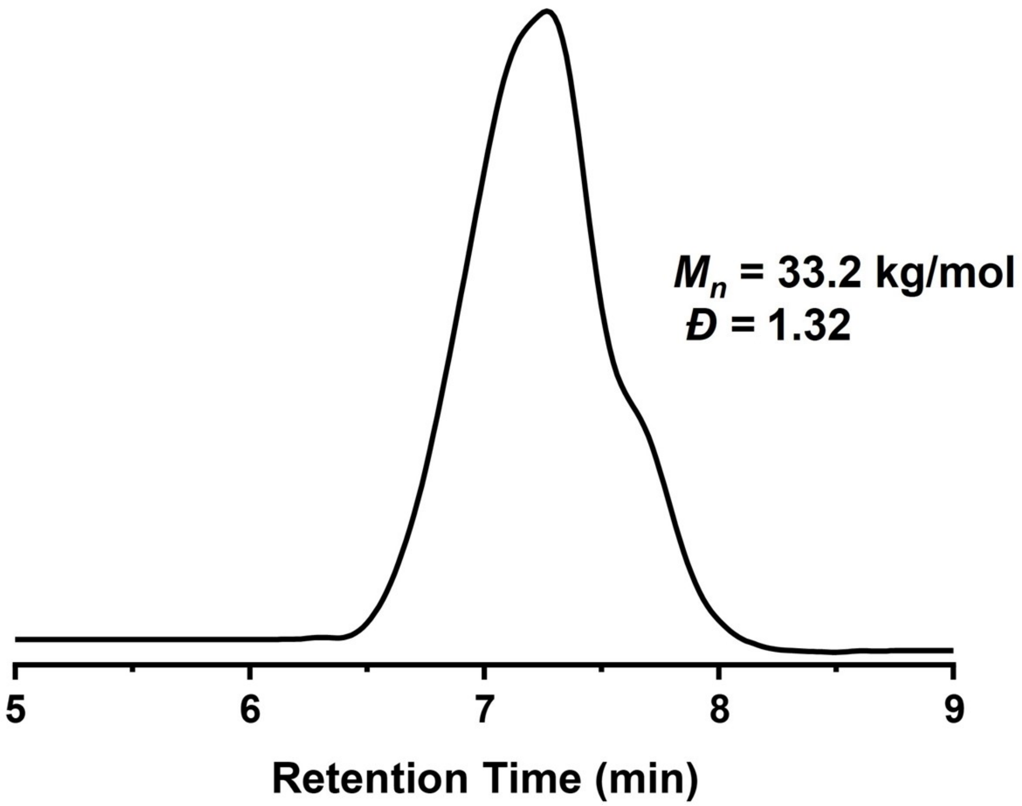

Fig. S20. GPC curve of P4-1.0 from Table 2, run 2

The minor low-molar-mass shoulders are assigned to incompletely chain-extended polyurethane oligomers or residual macromonomer-derived species, which are commonly observed in step-growth self-polyaddition of macromonomers under bulk conditions due to limited chain-end mobility and incomplete end-group conversion. The same assignment applies to the low-molar-mass shoulders seen in Figs. S21–S23.

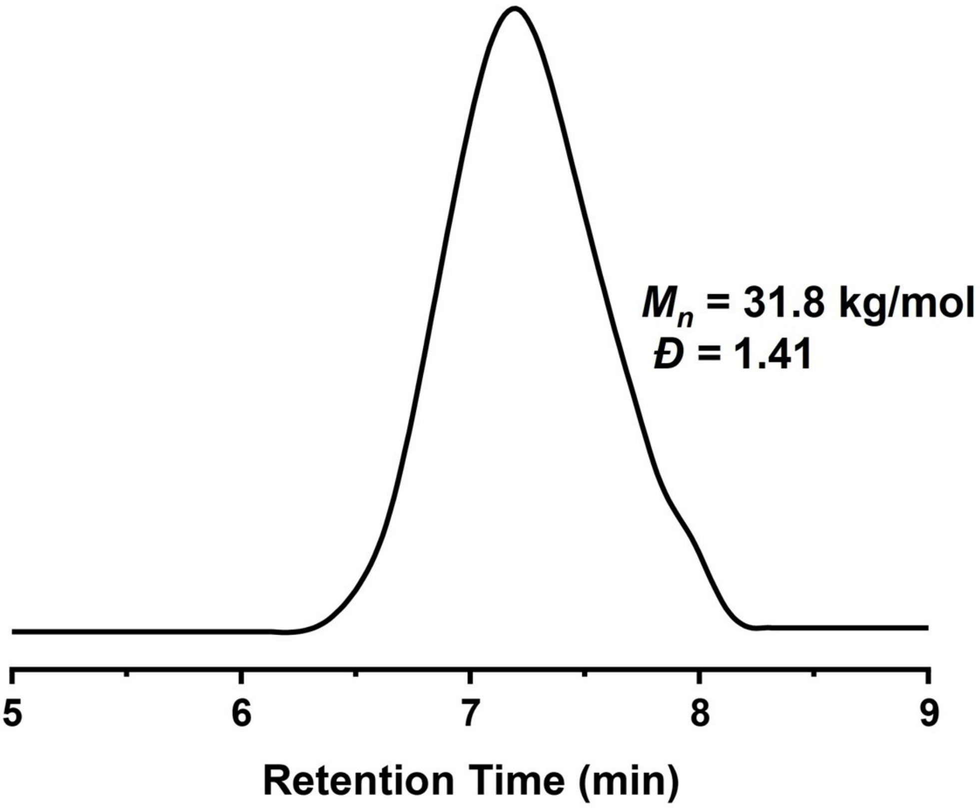

Fig. S21. GPC curve of P4-1.5 from Table 2, run 3

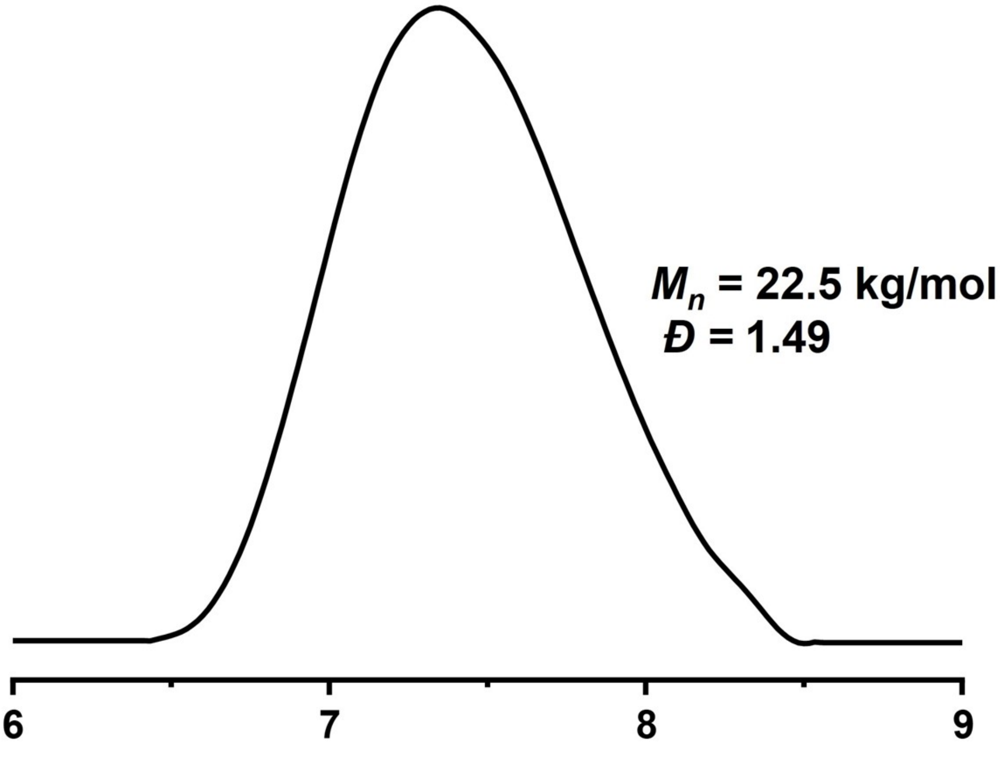

Fig. S22. GPC curve of P4-2.0 from Table 2, run 4

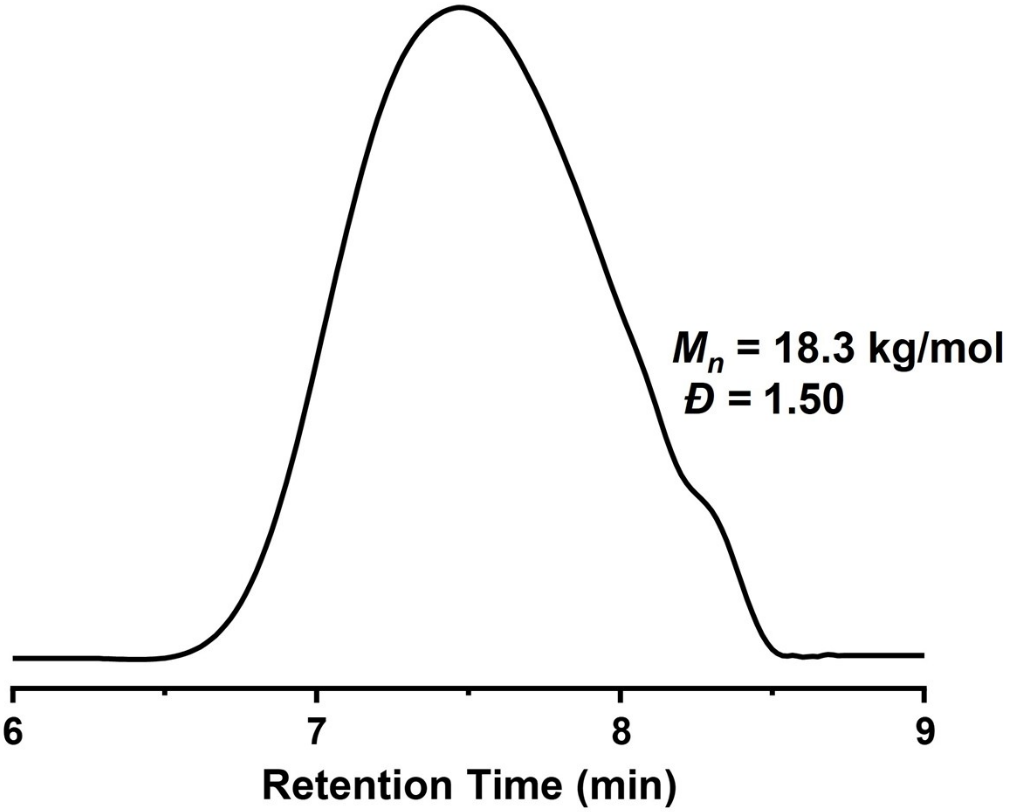

Fig. S23. GPC curve of P4-10.0 from Table 2, run 5

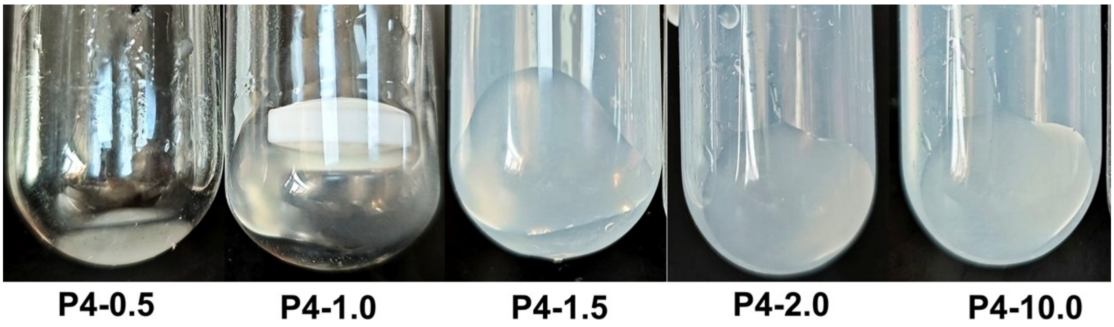

Fig. S24. The images of the obtained polymer P4