Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

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EXPERIMENTAL SECTION

Materials

Glycidyl phenyl ether (GPE; >99%, TCI) and *ε*-caprolactone were pretreated with CaH_2 overnight and distilled under reduced pressure and stored in argon. Lactide (LA; >98%, TCI) was purified through recrystallization using dry toluene at least three times and dried under high vacuum for 24 h. 1-(3,5-Bis(trifluoromethyl)phenyl)-3-phenylthiourea was prepared by literature method.[1] Tetrabutylammonium fluroride (TBAF) in tetrahydrofuran (THF) solution (1M) (TCI) used as received. Dichloromethane (CH_2Cl_2; >99.5%) was distilled from CaH_2 under an argon atmosphere.

Characterizations

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DRX-400 spectrometer in $CDCl_3$ at room temperature . The size exclusion chromatography (SEC) was equipped with a Wyatt Optilab rEX differential refractive index (DRI) detector (Wyatt Technology Corporation , USA) , a Wyatt DAWN HELEOS-II multi-angle light scattering (MALS) detector (laser at λ = 658 nm),a Waters Styragel HR 2 THF (5µm, 300 × 7.8 mm) column and a SSI 1500 pump ,using tetrahydrofuran (THF) as a polymer solvent and an eluent at a flow rate of 0.7 mL min^{-1} in 25 ℃. The molecular weight distribution was determined by a relative method using polystyrene as calibration standards. Matrix assisted laser desorption/ionization time-of-flight mass spectra (MALDI-ToF MS) were performed on a mass spectrometer (ultraflextreme; Bruker Co.) with Smartbeam/Smartbeam II modified Nd: YAG laser. Mass spectra of 500 shots were accumulated for the spectra at a 25 kV acceleration voltage. The polymer sample was dissolved in $CHCl_3$ at a concentration of 5 mg mL^{-1}, the matrix 2,5-DHB (2,5-dihydroxybenzoic acid) was dissolved in solution of trifluoroacetic acid and acetonitrile (volume ratio

= 70/30) in water (1%, 10 µL). Samples for the MALDI-ToF MS were prepared by mixing the matrix and polymer.

General procedure for Synthesis of poly(Glycidyl phenyl ether)-*block*-poly((lactide).

PGPE were synthesized according to the literature:[2] All polymerization were executed under argon atmosphere. The solution of tetrabutylammonium fluoride in tetrahydrofuran (0.1 mmol , 1 M) was added to the reaction flask. The tetrahydrofuran was evaporated under high vacuum for 1 h and GPE (30 mg, 2.0 mmol, 0.27ml) was added. The reaction mixture was stirred at 50 °C under an argon atmosphere . After 6 h, the flask cooled down to room temperature. Then a small amount of the reaction mixture was taken and then quenched with excess cool methanol for isolating PGPE which was analyzed by NMR and SEC. The remaining polymerization solution was not quenched and used for the next polymerization. Conv. (GPE): 99%. $M_{n,NMR}$ = 3.1 kg mol^{-1}; M_w/M_n = 1.10. ^{1}H NMR ($CDCl_3$, 400 MHZ): δ (ppm) 3.45-3.55 (1H, –OH); 3.60-3.80 (1H×n, $(–CH_2CH(CH_2OPh)O–)_n$), (2H×n, $(–CH_2CH(CH_2OPh)O–)_n$), and (2H, $FCH_2CH(O–)CH_2OPh$); 3.80-4.0 (2H×n, $(–CH_2CH(CH_2OPh)O–)_n$) and (2H, $FCH_2CH(O–)-CH_2OPh$); 4.40-4.60 (2H, $FCH_2CH(CH_2OPh)O–$); 6.70-7.30 (5H×(n+1), aromatic ring). ^{13}C NMR (CDCl3, 100 MHz): δ(ppm) 67.8 ($(–CH_2CH(O-)CH_2OPh–)_n$); 70.0 ($(–CH_2CH(O–)CH_2OPh)_n$) and ($FCH_2CH(O–)CH_2OPh$); 78.05 ($(–CH_2CH(O–)CH_2OPh)_n$); 78.26 ($FCH_2CH(O–)CH_2OPh$); 82.5 ($FCH_2–$); 114.74, 120.71, and 129.67 (methine carbon in aromatic ring); 158.55 (quaternary carbon in aromatic ring).

1-(3,5-Bis(trifluoromethyl)phenyl)-3-phenylthiourea (0.364 g, 0.1 mmol) was firstly added to the PGPE solution in the previous step without quenching. One hour later , lactide (0.288 g ,2mmol)was added to start polymerization of the second block. After 30 min , 0.1 ml of the reaction mixture was withdrawn and then excess benzoic acid was added for determining the monomer conversion by ^{1}H NMR measurements. When the conversion was above 90%, dry methanol was added to terminate the reaction. The diblock copolymer PGPE-*b*-PLA was obtained by reprecipitation in cold methanol and then dried under vacuum for 72 hours. Conv.: 97%. $M_{n,NMR}$ = 6.1 kg mol^{-1}; M_w/M_n = 1.13. ^{1}H NMR ($CDCl_3$, 400 MHZ): δ (ppm) 1.52 (3H , $(–COCH(CH_3)O–)$, 1.61(3H × 2m, $(–COCH(CH_3)O–)_{2m}$), 3.79 (1H×n, $(–CH_2CH(CH_2OPh)O–)_n$), (2H×n, $(–CH_2CH(CH_2OPh)O–)_n$), and (2H, $FCH_2CH(O–)CH_2OPh$), 3.96 (2H×n, $(–CH_2CH(CH_2OPh)O–)_n$) and (2H, $FCH_2CH(O–)CH_2OPh$), 4.37 (1H , $(–COCH(CH_3)O–)$, 4.40-4.60

(2H, $FCH_2CH(CH_2OPh)O–$); 5.18 (1H × 2m ($–OCOCH(CH_3)O(COCH(CH3)O–)_{2m}$), and (1H,–$OCOCH(CH_3)O(COCH(CH3)O–)_{2m}$); 5.32 (1H, $–CH_2CH(O–)CH_2PhCOCH(CH_3)O–$) 6.80–7.30 (5H, aromatic). ^{13}C NMR (CDCl3, 100 MHz): δ(ppm) 16.52 ($(–COCH(CH_3)O–)_{2m}$); 20.10 ($–COCH(CH_3)O–$); 66.49 ($(–CH_2CH(O–)CH_2OPh–)_n$); 67.64 ($(–CH_2CH(O–)CH_2OPh)_n$) and ($FCH_2CH(O–)CH_2OPh$); 68.80 (–$COCH(CH_3)O–)_{2m}$); 78.02 ($(–CH_2CH(O–)CH_2OPh)_n$); 78.14 ($FCH_2CH(O–)CH_2OPh$); 82.5 ($FCH_2–$); 114.35, 120.62, and 129.22 (methine carbon in aromatic ring); 158.48 (quaternary carbon in aromatic ring); 169.38 ($(–COCH(CH_3)O–)_{2m}$); 169.44 ($–CH_2CH(O–)CH_2PhCOCH(CH_3)O–$); 174.90 ($–COCH(CH_3)O–$).

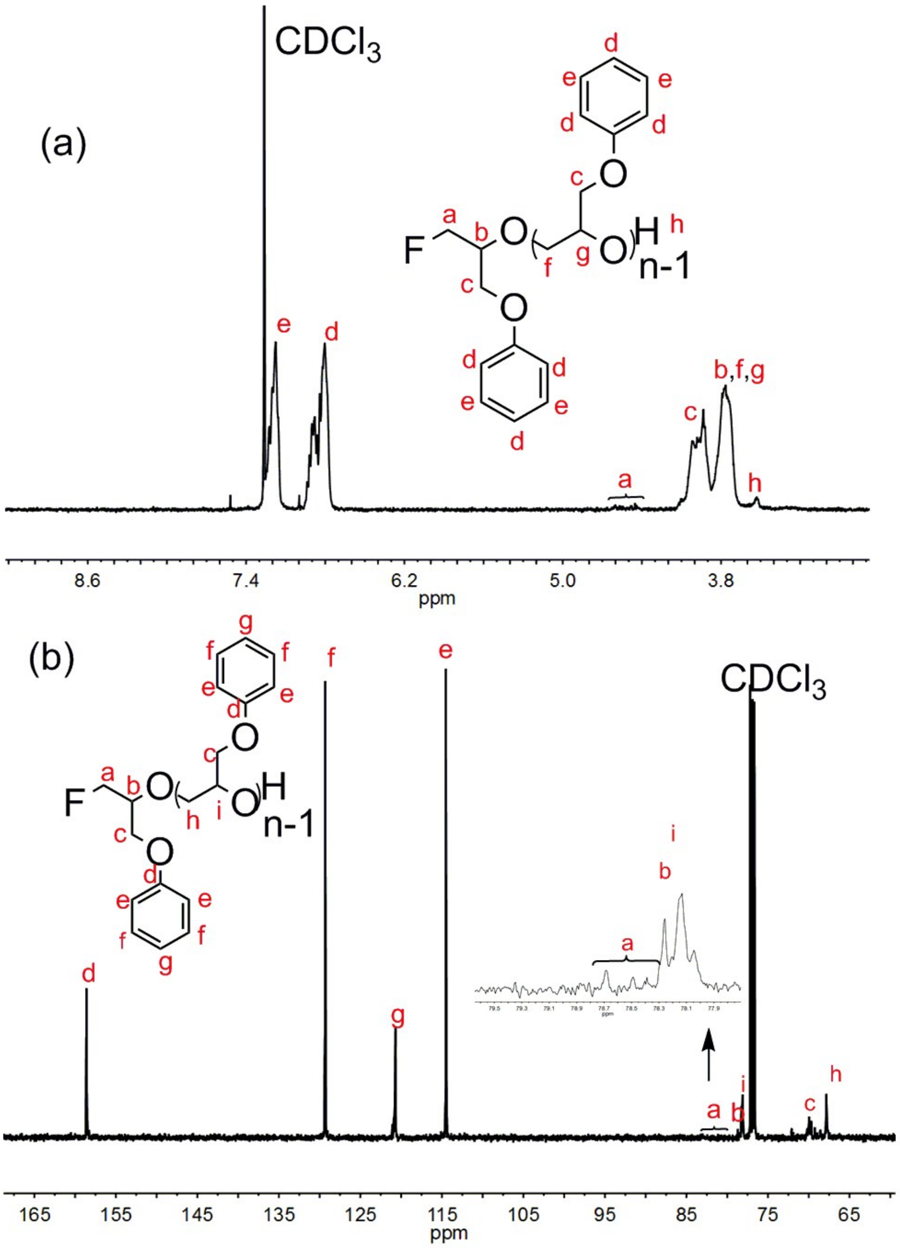
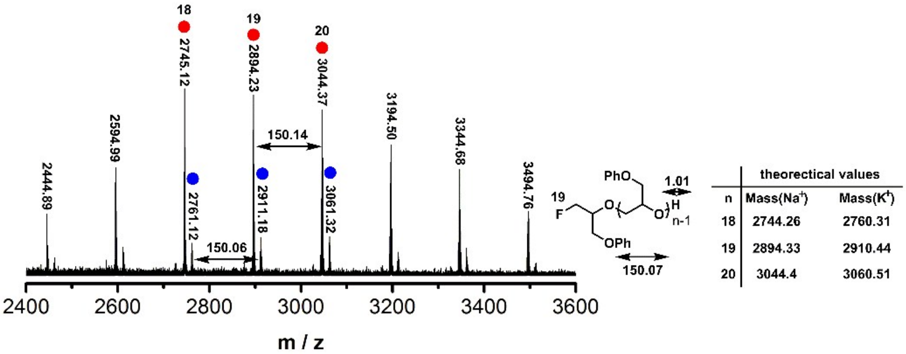


Figure S1. The ^1H NMR (a) and ^{13}C NMR (b) spectra (in $CDCl_3$) of PGPE.



n	theorectical values Mass(Na$^+$)	Mass(K$^+$)
18	2744.26	2760.31
19	2894.33	2910.44
20	3044.4	3060.51

Figure S2. MALDI-ToF MS spectrum of PGPE from TBAF-initiated ring-opening polymerization of GPE.

REFERENCES

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(2) Morinaga, H.; Ochiai, B.; Endo, T., Metal-free ring-opening polymerization of glycidyl phenyl ether by tetrabutylammonium fluoride. *Macromolecules* **2007,** *40,* 6014-6016.