

Reversible Aminolysis: A New Concept for Postpolymerization Modification

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SUPPORTING INFORMATION

Experimental Section

Materials

An aqueous 12N HCl solution and ethanol (99.5%) was purchased from Kanto Chemical Co., Ltd. and used as received. Poly(ethyl 2,2-difluoro-2-(4-vinylphenoxy)acetate) (PSt-OCF₂CO₂Et) and poly(*n*-hexyl 2,2-difluoro-2-(4-vinylphenoxy)acetamide) (PSt-OCF₂CONH-hex) were prepared according to published protocol.¹ All other chemicals were commercially available and used without further purification unless otherwise stated.

Instruments

All the ¹H and ¹⁹F NMR spectra in deuterated solvents were recorded on Bruker 500 MHz FT-NMR spectrometer, and the chemical shifts (δ) are given in ppm with either the solvent peak or tetramethylsilane as the internal standard. The ¹⁹F NMR spectra were calibrated with an internal standard (C₆F₆ = 0 ppm). The SEC measurements were performed at 40 °C and a flow rate of 0.35 mL·min⁻¹ in dimethylformamide (DMF) containing 10 mmol·L⁻¹ LiCl on a Waters gel permeation chromatography e2695 system embedded with a column (4.6 × 150 mm Tosoh TSKgel SuperMultiporeHZ-M). The M_n and D values of the polymers were calculated with polystyrene calibration. The standard IR spectra were recorded using an Agilent Cary 630 spectrometer equipped with an ATR unit.

Synthesis

Typical procedure for the acid-mediated ethanolysis of PSt-OCF₂CONH-hex: To a test tube was added PSt-OCF₂CONH-*n*-hexyl (450 mg, 1.57 mmol, 1.0 eq.), PTSA (1.49 g, 7.84 mmol, 5.0 eq.), ethanol (4.5 mL), and 1,2-dichloroethane (0.9 mL) and allowed to react at 80 °C for 72 hours under open conditions. The target compound was obtained by reprecipitation into ethanol.

Yield: 312 mg (82.1 %), SEC; 61.2 kg·mol⁻¹, D ; 1.58

Kinetic measurements for post-polymerization modification reaction: Under an open condition, PSt-OCF₂CONH-hexyl (300 mg, 1.05 mmol, 1.0 eq.), PTSA (1.00 g, 5.23 mmol, 5.0 eq.), ethanol (3.0 mL) and 1,2-dichloroethane (0.6 mL) were added to a vial and allowed to react at 80 °C. An aliquot of

the reaction solution in the vial was collected after each predetermined reaction time and ^{19}F NMR measurements were performed. The obtained data were analyzed by using MestRenova software.

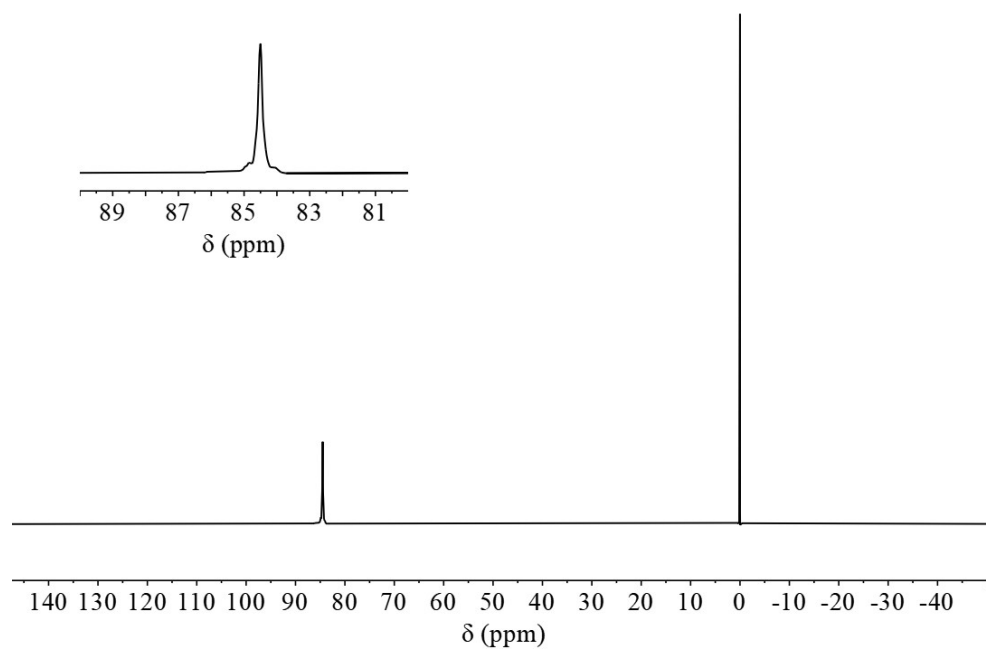


Figure S-1. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt-OCF₂CONH-hex (run 1 in Table 1).

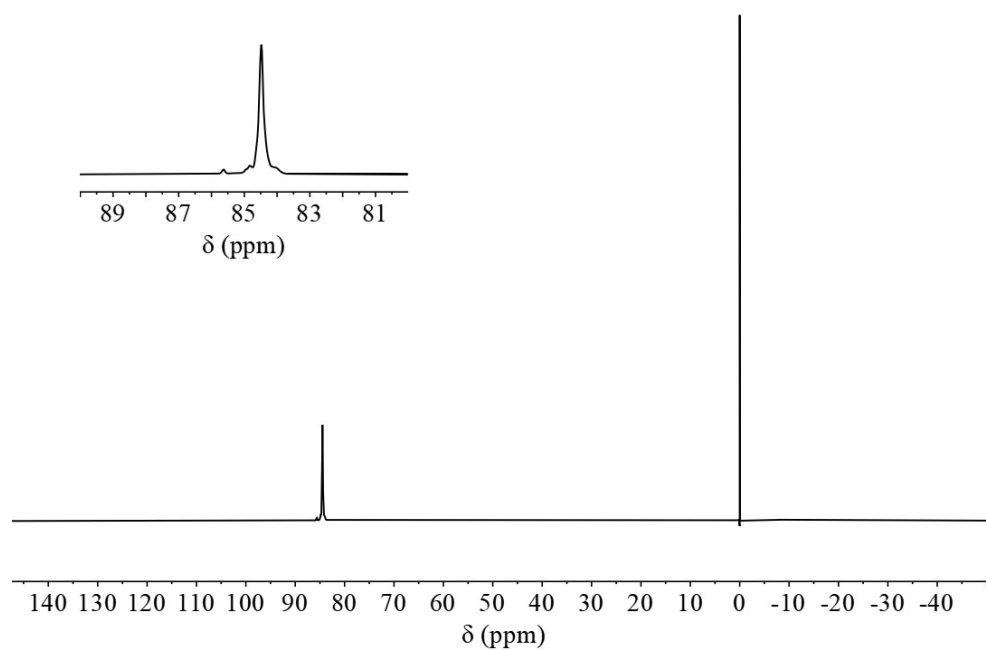


Figure S-2. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt-OCF₂CONH-hex (run 2 in Table 1).

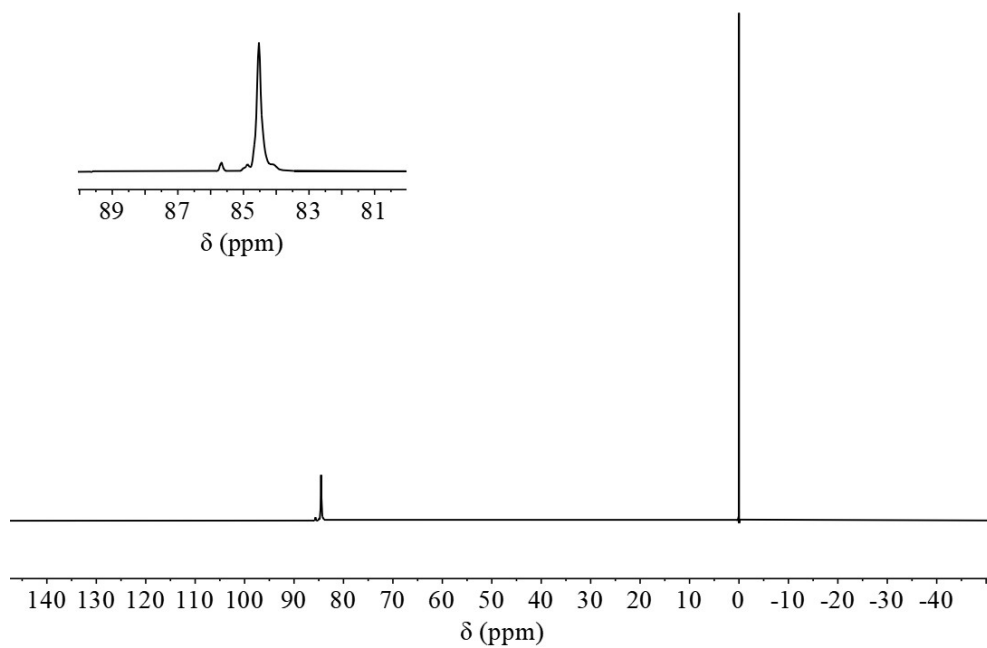


Figure S-3. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt- OCF_2CONH -hex (run 3 in Table 1).

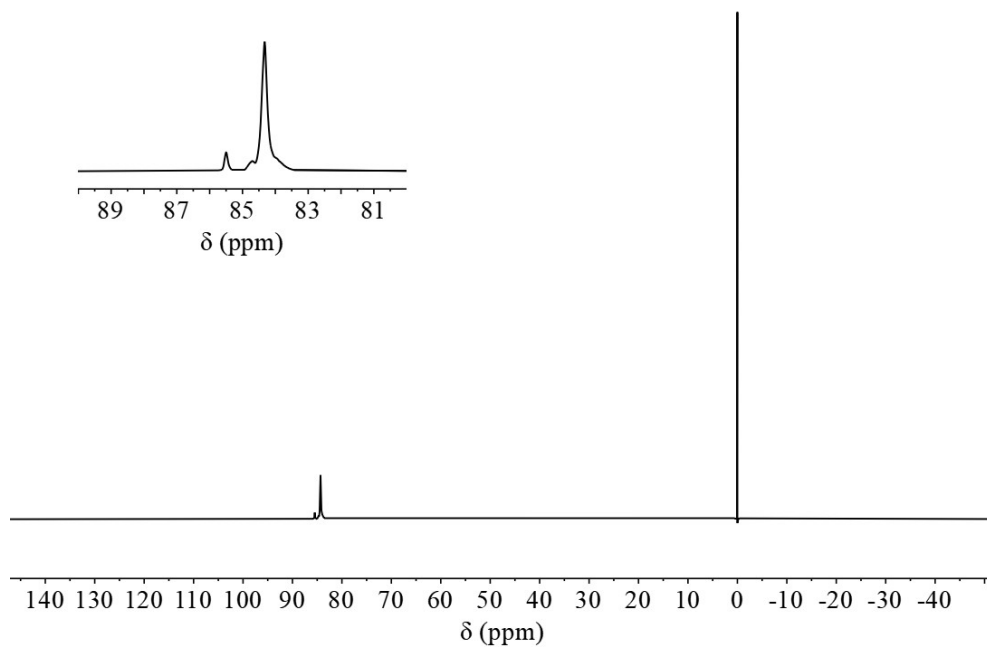


Figure S-4. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt- OCF_2CONH -hex (run 4 in Table 1).

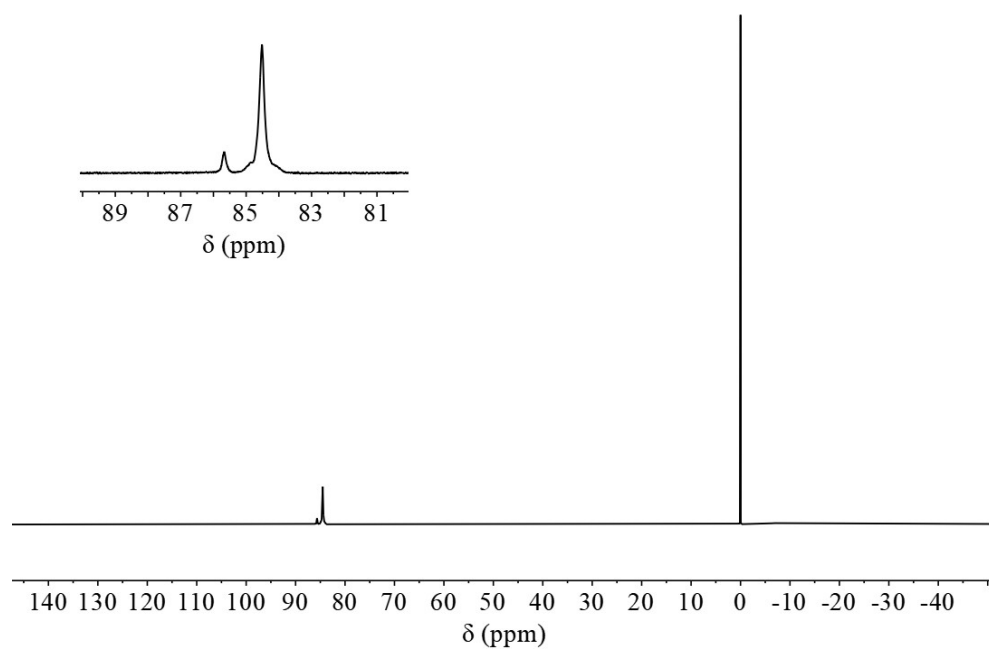


Figure S-5. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt-OCF₂CONH-hex (run 5 in Table 1).

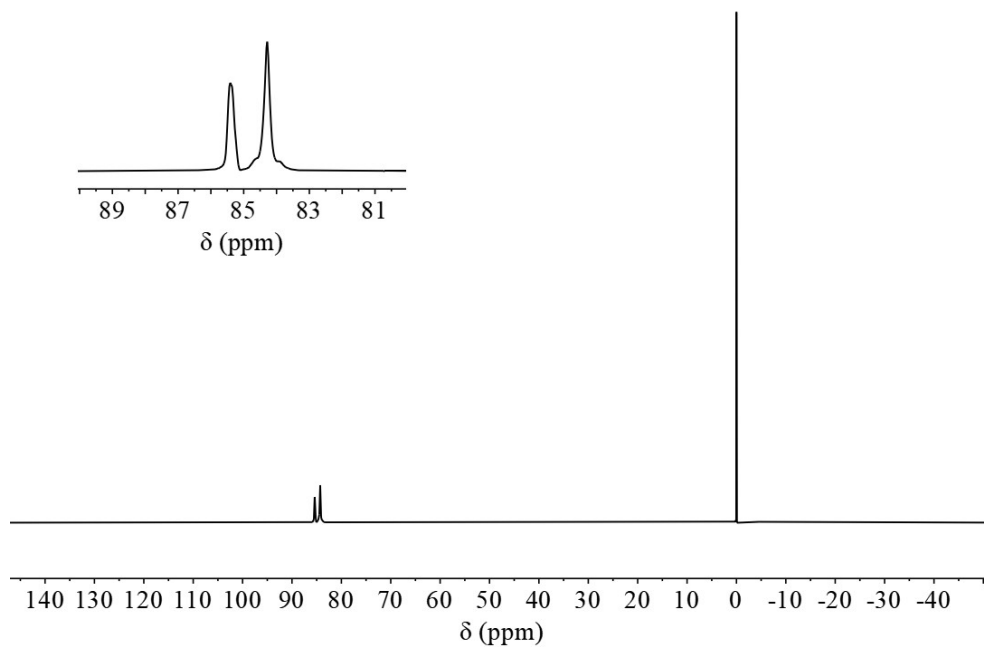


Figure S-6. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt-OCF₂CONH-hex (run 6 in Table 1).

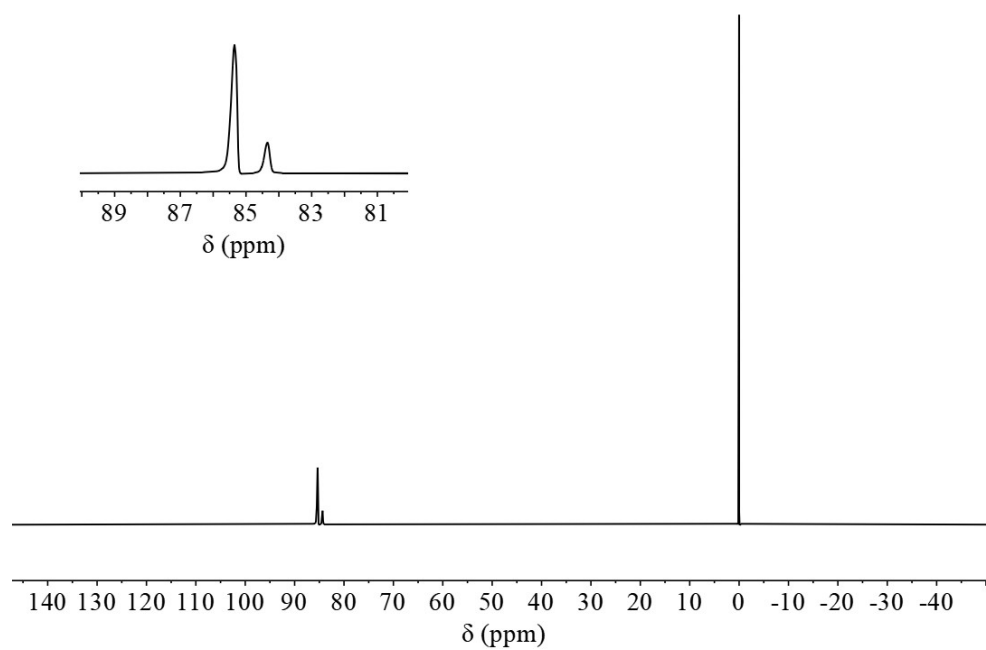


Figure S-7. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt- OCF_2CONH -hex (run 7 in Table 1).

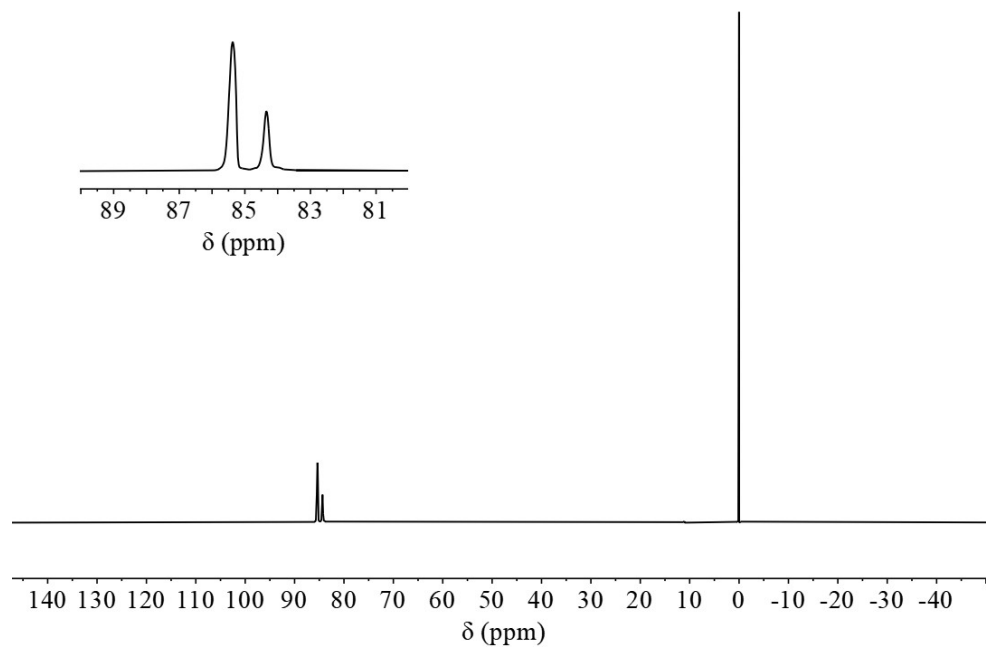


Figure S-8. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt- OCF_2CONH -hex (run 8 in Table 1).

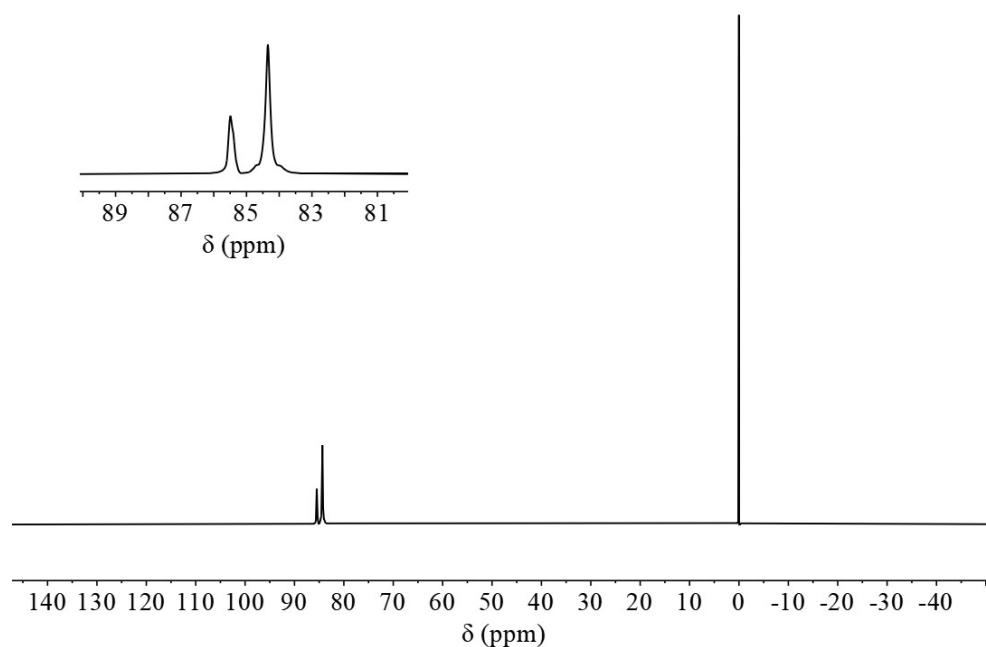


Figure S-9. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt- OCF_2CONH -hex (run 9 in Table 1).

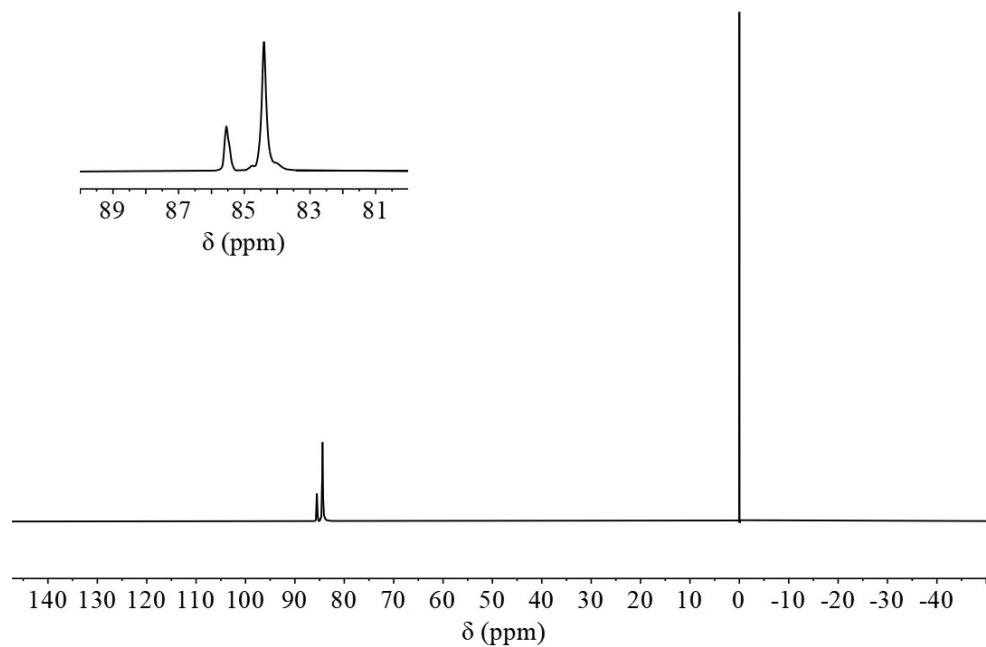


Figure S-10. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt- OCF_2CONH -hex (run 10 in Table 1).

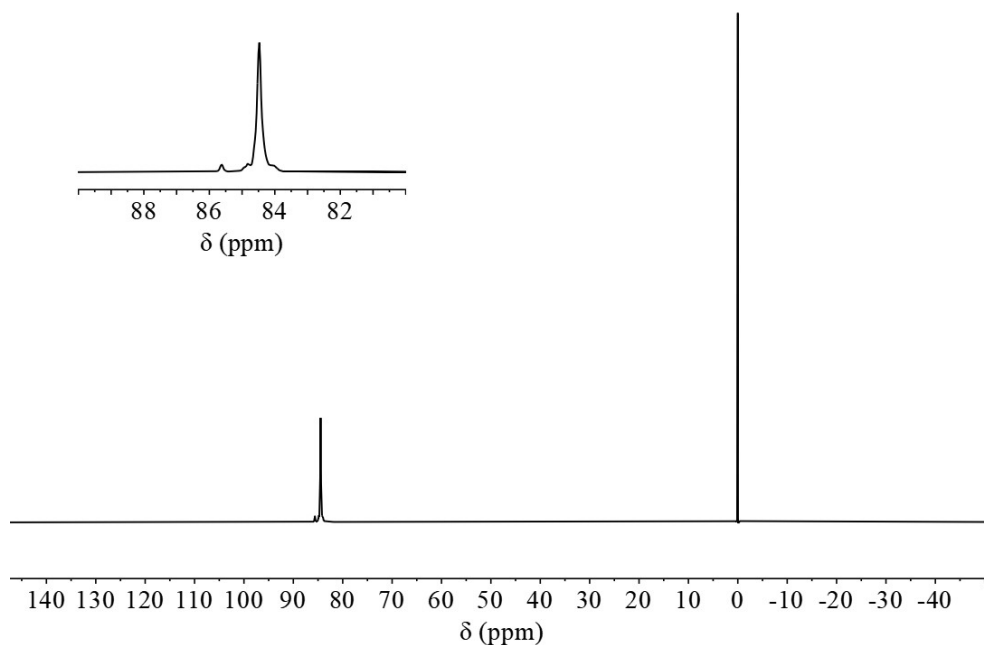


Figure S-11. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer after acid-mediated ethanolysis of PSt-OCF₂CONH-hex (run 11 in Table 1).

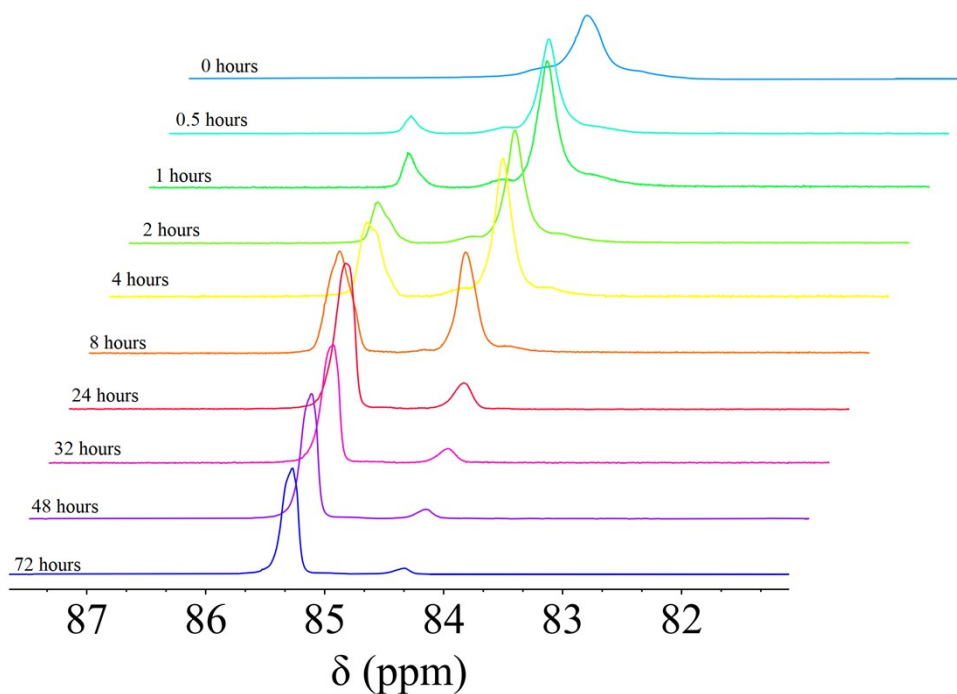


Figure S-12. Waterfall ^{19}F NMR spectra in CDCl_3 of the kinetic analysis for acid-mediated ethanolysis of PSt-OCF₂CONH-hex (Figure 1).

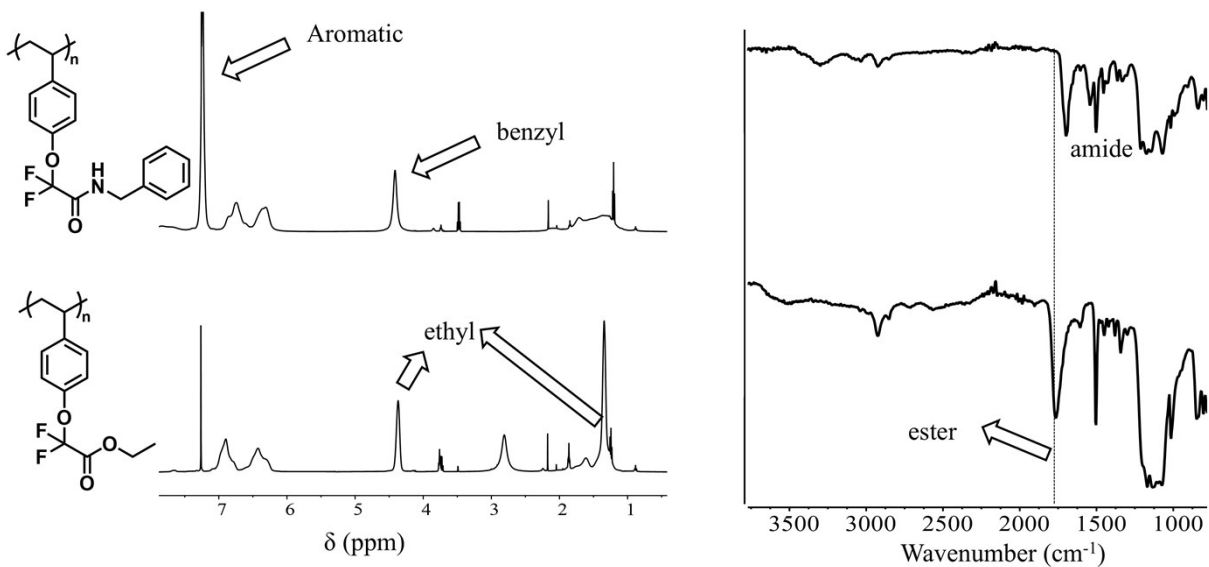


Figure S-13. ¹H NMR in CDCl₃ and ATR-mode FT-IR spectra of the polymers before and after the acid-mediated ethanolysis of the polymeric amides derived from benzylamine.

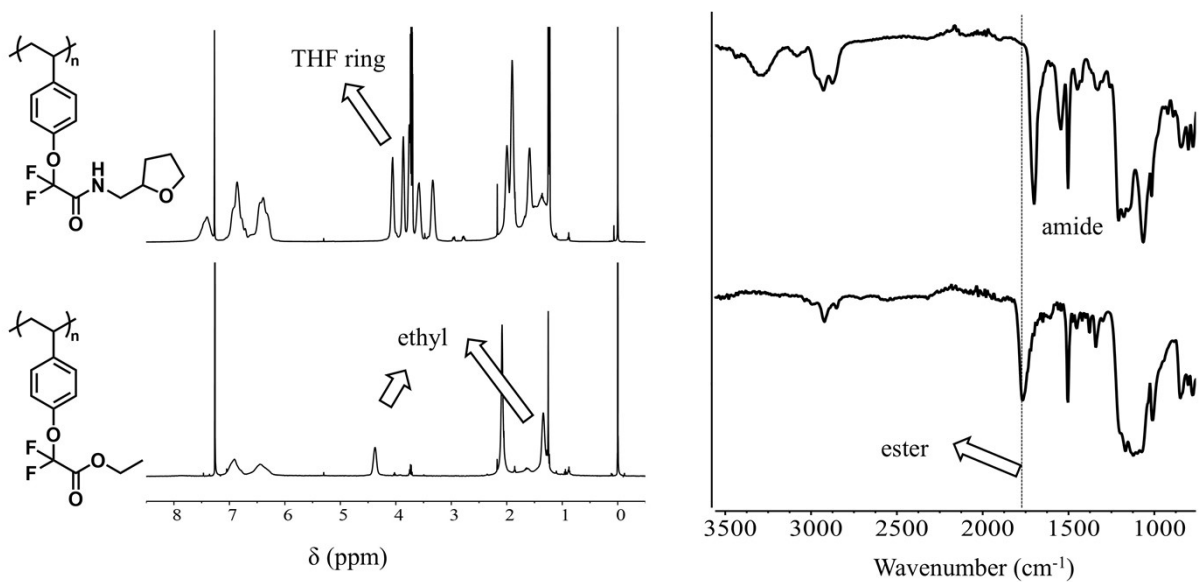


Figure S-14. ¹H NMR in CDCl₃ and ATR-mode FT-IR spectra of the polymers before and after the acid-mediated ethanolysis of the polymeric amides derived from tetrahydrofurfurylamine.

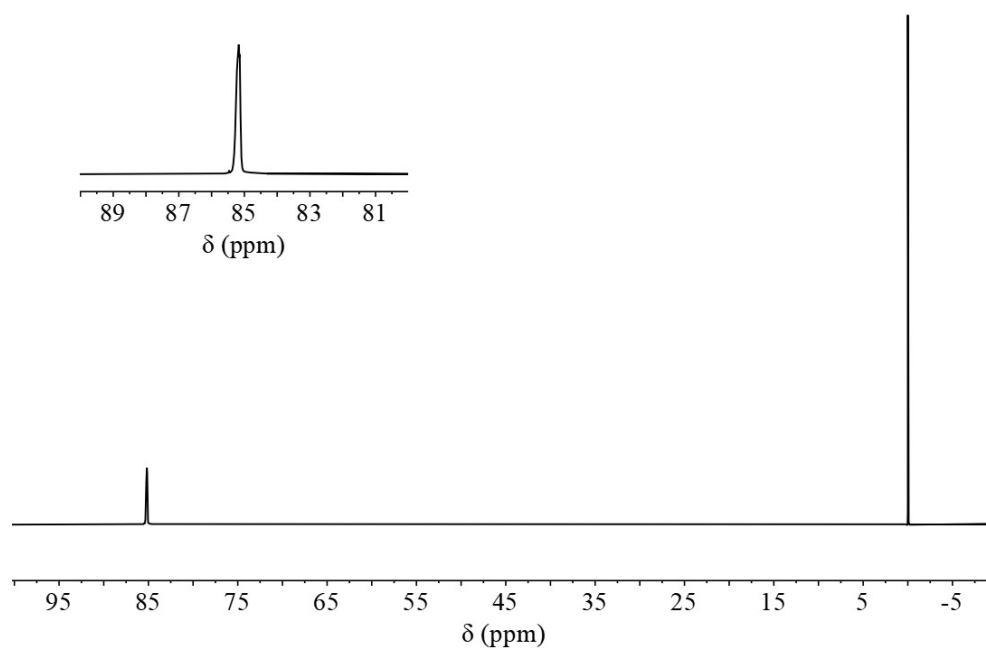


Figure S-15. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer via the sequential PPM at the stage of A depicted in Figure 3.

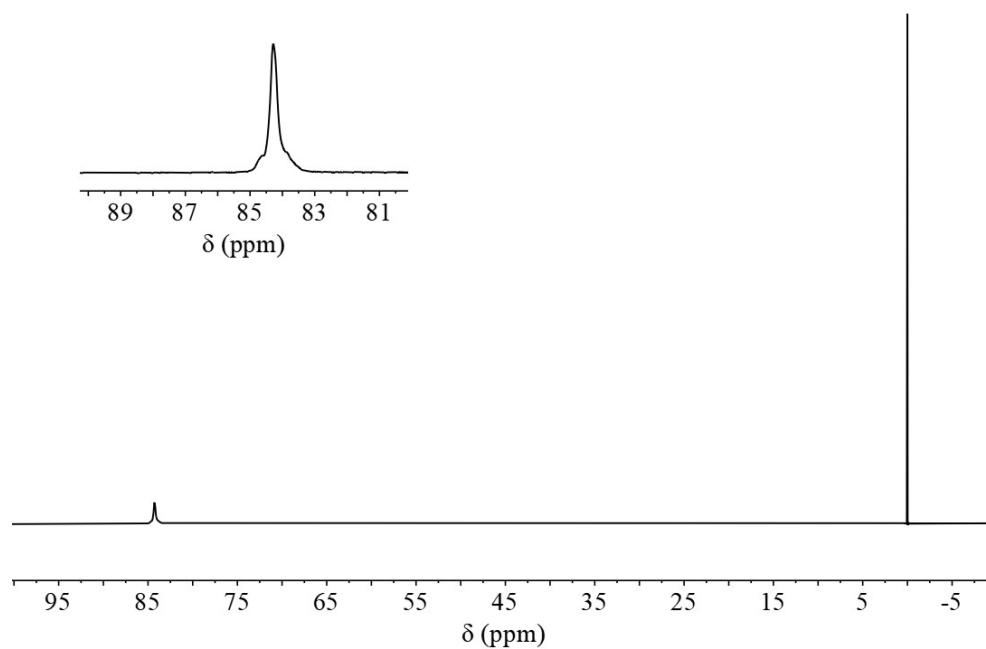


Figure S-16. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer via the sequential PPM at the stage of B depicted in Figure 3.

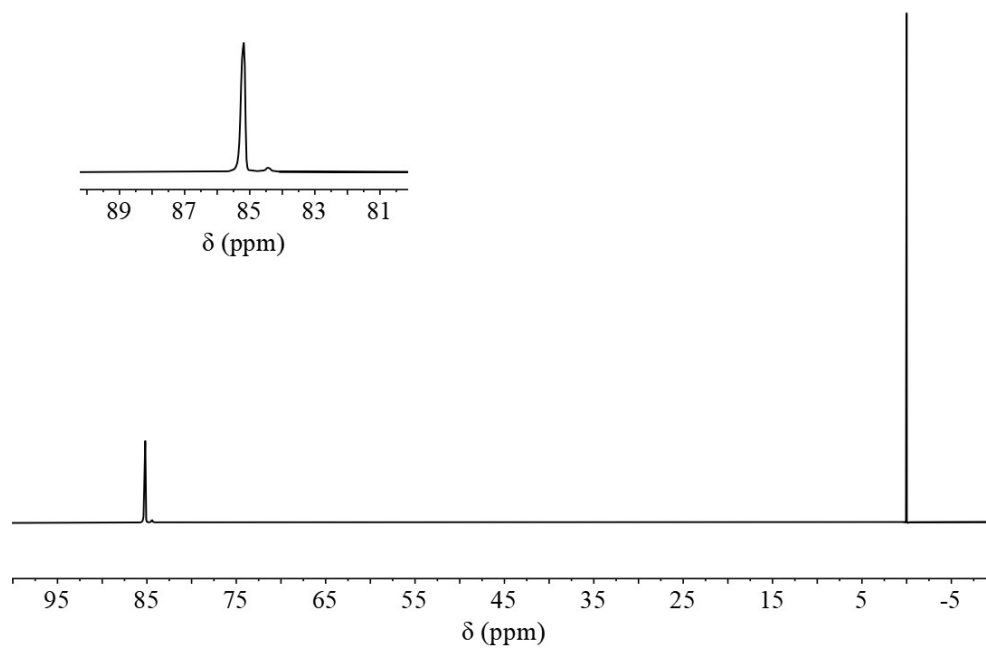


Figure S-17. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer via the sequential PPM at the stage of C depicted in Figure 3.

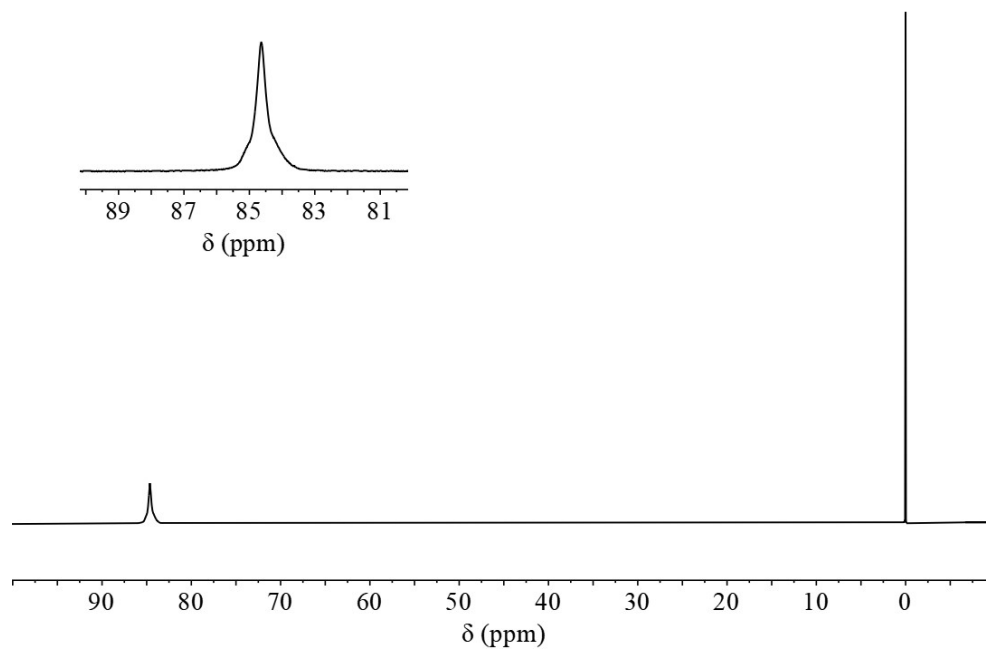


Figure S-18. ^{19}F NMR spectrum in CDCl_3 of the obtained polymer via the sequential PPM at the stage of D depicted in Figure 3.

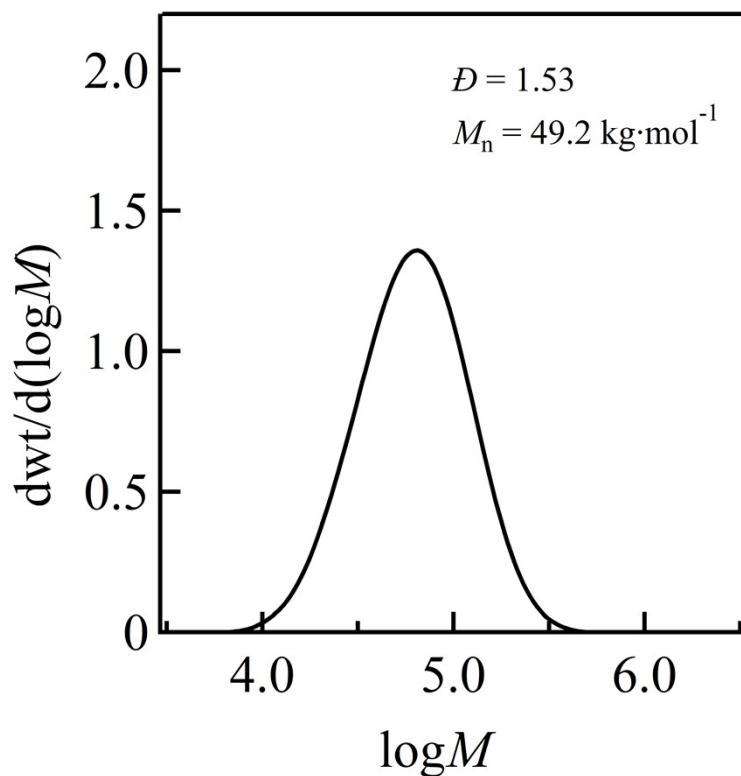


Figure S-19. SEC trace of the obtained polymer via the sequential PPM at the stage of A depicted in Figure 3.

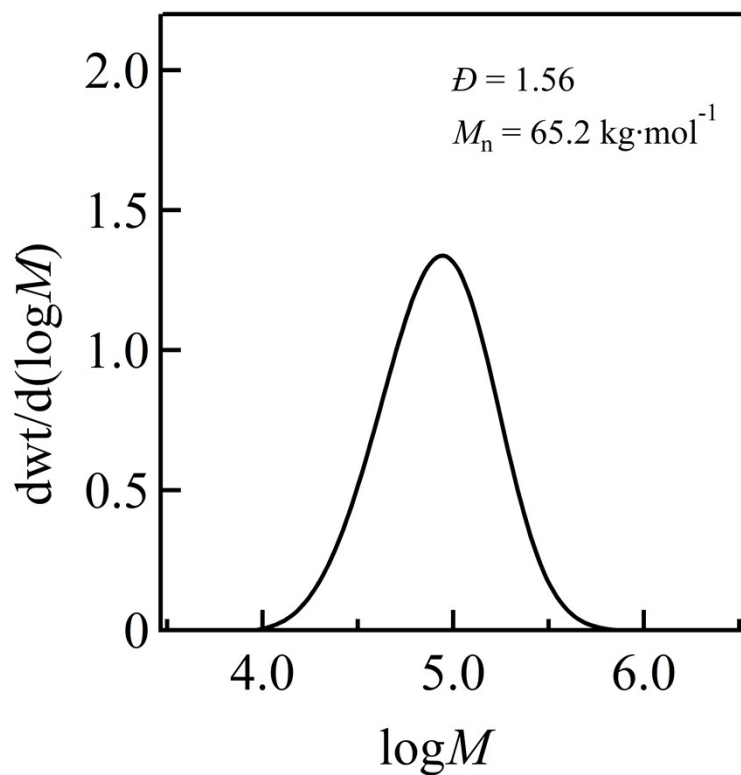


Figure S-20. SEC trace of the obtained polymer via the sequential PPM at the stage of B depicted in Figure 3.

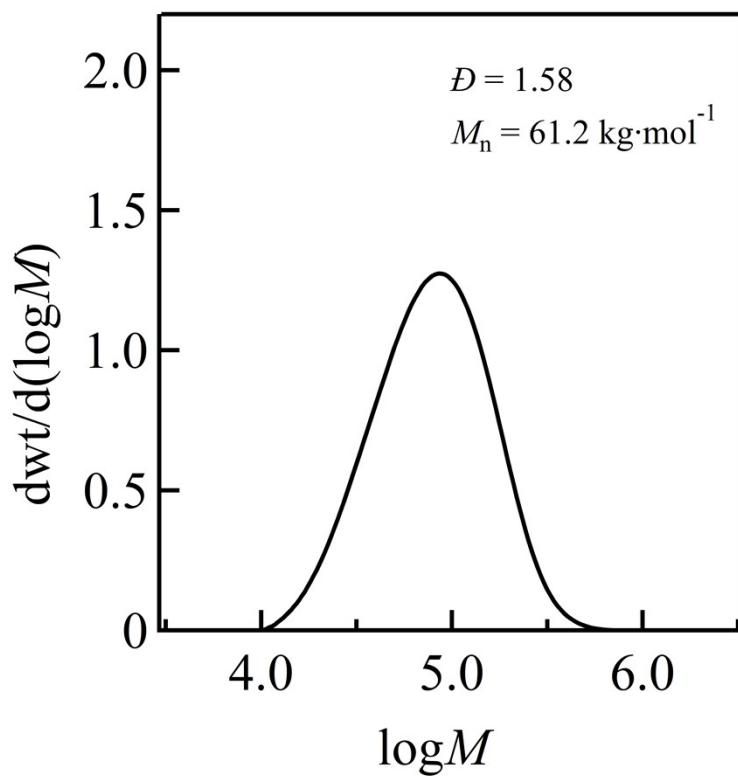


Figure S-21. SEC trace of the obtained polymer via the sequential PPM at the stage of C depicted in Figure 3.

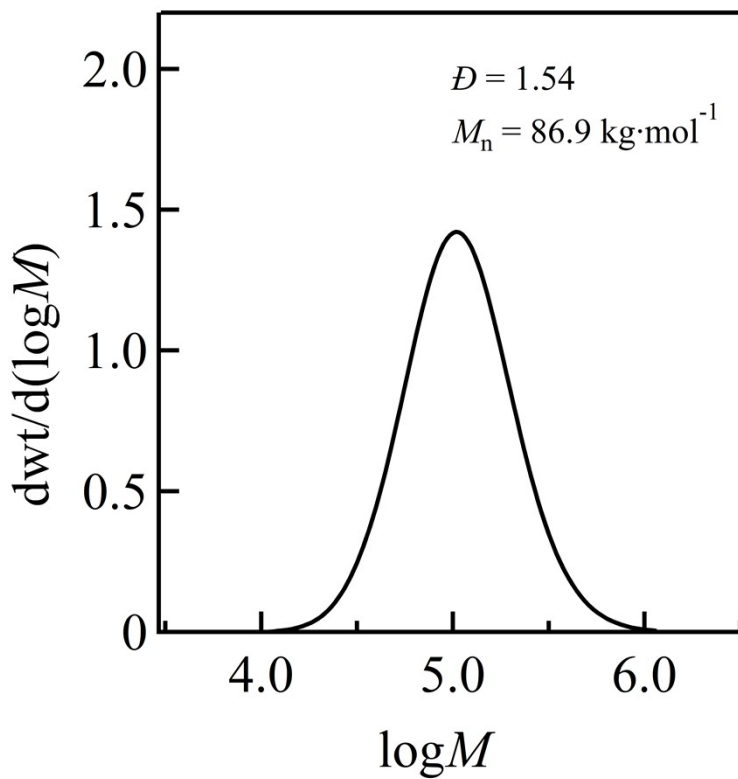


Figure S-22. SEC trace of the obtained polymer via the sequential PPM at the stage of D depicted in Figure 3.

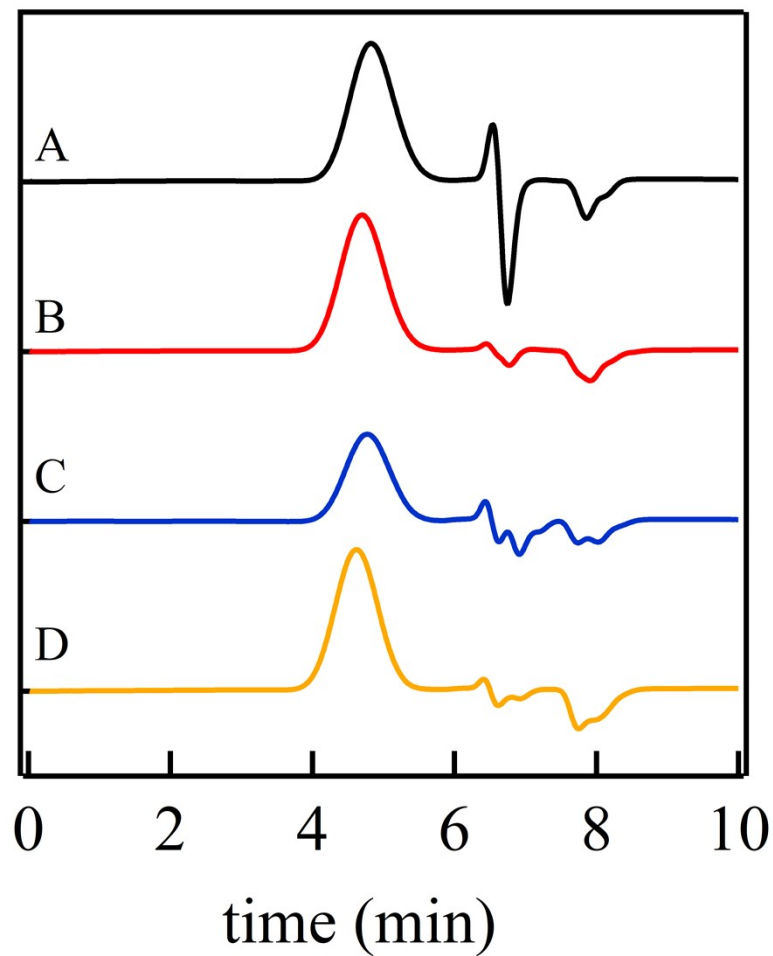


Figure S-23. Original SEC charts of the obtained polymers (A,B,C, and D) via the sequential PPMs depicted in Figure 3.

References

1. R. Kakuchi, K. Matsubara, K. Fukasawa and H. Amii, *Macromolecules*, 2021, **54**, 6204-6213.