

A New Strategy for the Synthesis of Fluorinated Polyurethane

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1. Synthesis of S-benzyl O-ethyl dithiocarbonate (BEDTC)

BEDTC was synthesized according to a previous report.¹ The synthesis was conducted by stirring 40 mL ethanol and 5.6 g KOH (0.10 mol) until a clear solution was formed. Then, 20 mL CS₂ (0.33 mol) was slowly added into the solution, and the mixture was stirred for 10 h at room temperature before excess CS₂ was distilled off at 70 °C. Then, 10 mL benzyl chloride (0.087 mol) in 20 mL of ethanol was added to the residual solution, and the mixture was further stirred at 60 °C for 5 h. After removal of the inorganic salt and most of the ethanol, 50 mL water was added, and the solution was extracted with diethyl ether (3×40 mL). The combined organic layer was dried over anhydrous Na₂SO₄. Removal of the inorganic salt and evaporation of the solvent afforded a yellow oil product: 12.1 g, 65.8%. ¹H and ¹³C NMR spectra are shown in Figure S1 and Figure S2, respectively.

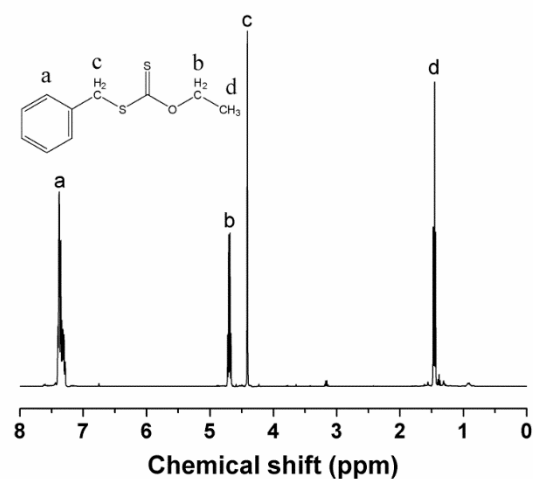


Figure S1. ^1H NMR spectrum of BEDTC recorded in CDCl_3 at room temperature.

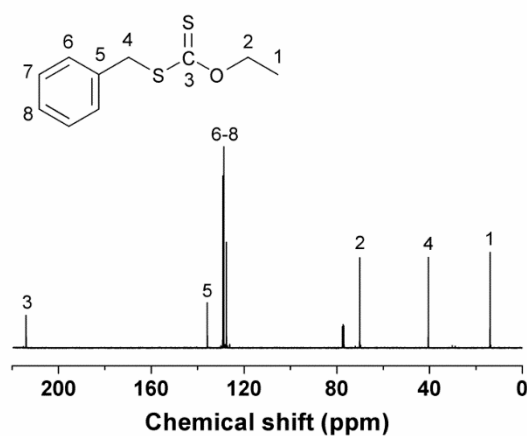


Figure S2. ^{13}C NMR spectrum of BEDTC recorded in CDCl_3 at room temperature.

2. Chemical shifts of the copolymers in ^1H NMR spectra

Poly(CTFE-alt-BVE) (δ =ppm): 4.52 (m, 1H), 3.73 (m, 2H), 2.75 (m, 2H), 1.59 (m, 2H), 1.40 (m, 2H), 0.89 (m, 3H).

Poly(CTFE-alt-BVE)-*b*-PVAc (δ =ppm): 4.81 (m, 1H), 4.50 (m, 1H), 3.71 (m, 2H),

2.74 (m, 2H), 1.99 (s, 3H), 1.75 (m, 2H), 1.55 (m, 2H), 1.38 (m, 2H), 0.85 (m, 3H).

Poly(CTFE-alt-BVE)-*b*-PVA (δ =ppm): 4.46 (m, 1H), 3.92 (m, 1H), 3.70 (m, 2H),
2.72 (m, 2H), 1.52 (m, 2H), 1.40 (m, 2H), 1.35 (m, 2H), 0.84 (m, 3H).