Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic Supplementary Information

Xanthate-Mediated Living/Controlled Radical Polymerization of Hexafluoropropylene and Butyl Vinyl Ether under ^{60}Co γ-ray Irradiation and Preparation of Fluorinated Polymer End-Capped with a Fluoroalkyl Sulfonic Acid

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Materials. Butyl vinyl ether (BVE) (Hubei Xinjing New Materials Co., Ltd, China) was dried with CaH_2, and distilled under reduced pressure before use. Vinyl acetate (VAc) (Shanghai Chemical Co., China) was purified by passing through a basic alumina column, and subsequently distilled. Hexafluoropropylene (HFP) was purchased from Zhejiang Juhua Co., Ltd, China. m-Chloroperoxybenzoic acid (m-CPBA) was purchased from Anhui Jinao Chemical Co., Ltd, China. Methyl acetate was refluxed and distilled over CaH_2. All other chemicals were used as received unless otherwise noted.

Instrumentation. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker DPX-400 spectrometer, using $CDCl_3$ as a solvent. The values of the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by means of a Waters 150C gel permeation equipped with 10^3, 10^4, 10^5 Å Waters Ultrastyragel columns and light scattering detector, using THF (1.0mL/min) as the eluent, and the calibration was carried out with polystyrene standards. FT-IR spectra were recorded on a Bruker VECTOR-22 infrared spectrometer.

Synthesis of ethyl 2-(ethoxycarbonothioylthio) acetate (EECTTA). EECTTA was synthesized according to the literature[1]. Briefly, ethyl bromoacetate (1eq) was added by portion to a yellow suspension of O-ethylxanthic acid potassium salt (1eq) in acetone (1M). The beige reaction mixture was stirred overnight at room temperature and concentrated. Purification on silica gel (petrol ether/ethyl acetate=5:1) afforded desired compound as a yellow oil with a yield of 86%, and the ^{1}H NMR spectrum is shown in Figure S1.

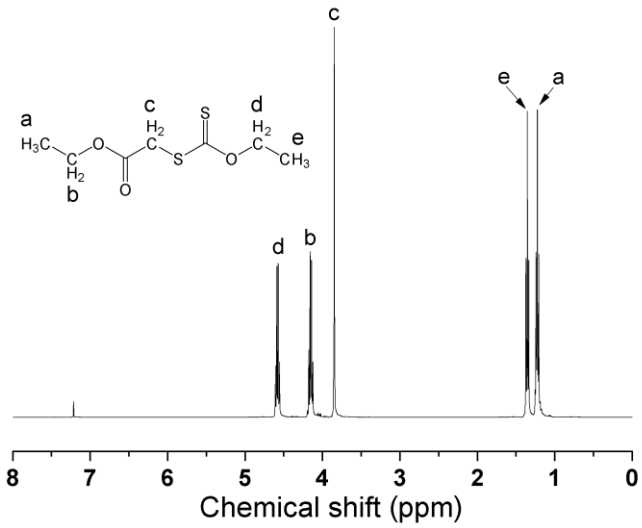

Figure S1. ^{1}H NMR spectrum of EECTTA ($CDCl_3$ as solvent).

Polymerization. The polymerization was performed in a 30 mL stainless steel autoclave equipped with a manometer, a magnetic stirrer, and a safety inlet valve. EECTTA (16.4 mg, 0.079 mmol), BVE (1.0ml, 7.9 mmol), and methyl acetate (5.0 mL) were introduced into the autoclave and bubbled with argon for 3 min. Then the vessel was closed and immerged into the liquid nitrogen for 15 min. After 7 vacuum-nitrogen cycles were applied to remove the oxygen, HFP (2.4 g, 16 mmol) was condensed into the autoclave and assessed by double weighing. The polymerization was carried out at room temperature under ^{60}Co γ-ray irradiation (145 Gy/min) for the desired time, and then quenched by cooling with ice water. The unreacted HFP was slowly vented. The solution was concentrated and precipitated into cold methanol. The polymer was finally dried under vacuum at 50 ^{o}C and the conversion of the monomer was determined by gravimetry. Theoretical values of the molecular weight were calculated according to equation 1.

$$M_{n,th}=([BVE]_0/[EECTTA]_0)\times conversion\times(M_{BVE}+M_{HFP})+M_{EECTTA} \quad (1)$$

Here $[BVE]_0/[BEDTC]_0$ is the initial molar ratio of BVE to EECTTA. M_{BVE}, M_{HFP}, and M_{EECTTA} stand for the molecular weights of BVE, HFP, and EECTTA respectively.

Chain extension reaction. A glass tube was charged with the fluorinated copolymer (0.442 g, 0.034 mmol), AIBN (1.3 mg, 0.008 mmol), VAc (1.26 mL, 13.6 mmol), and ethyl acetate (2.0 mL). Then it was degassed by three cycles of freeze-vacuum-thaw. After sealed under vacuum, the tube was placed into an oil bath. The reaction mixture was stirred for 8 h at 70 ^{o}C. Then the tube was cooled down by ice water to stop the reaction and the solution was precipitated into ethanol. The resultant copolymer was collected and dried under vacuum at 50 ^{o}C.

Transformation of end-group. The fluorinated copolymer (1.0 g) was dissolved in 5.0 mL acetone and m-CPBA at a certain molar ratio to the xanthate group was added to the solution. The reaction was carried out at 0 ^{o}C for predetermined time. The polymer was isolated and purified by precipitation of the polymer solution into ethanol for twice. The $-SO_3H$ end-group concentration of the treated polymer was determined by titration. We have done a preliminary experiment to optimize the molar ratio of m-CPBA to the fluorocopolymer for the the oxidation reaction, and the result was shown in Figure S2. As can be seen, the $-SO_3H$ molar content reach a highest value of about 75%, when 10 fold of m-CPBA was used. Judging by this, we choose 10 fold molar ratio for our subsequent kinetic study.

Titration of the -SO_3H end-group. In a standard experiment, a solution of 0.5 g polymer in 15 mL toluene was titrated with a 0.01 M NaOH solution in methanol/toluene (v/v=1:95) using phenolphthalein as an indicator. For comparison, the same samples were measured by excessive titration by 1 mL of 0.01 M NaOH, and reverse titration with 0.01 M benzoic acid in methanol/toluene (v/v=1:95) after stirring for 1 min.

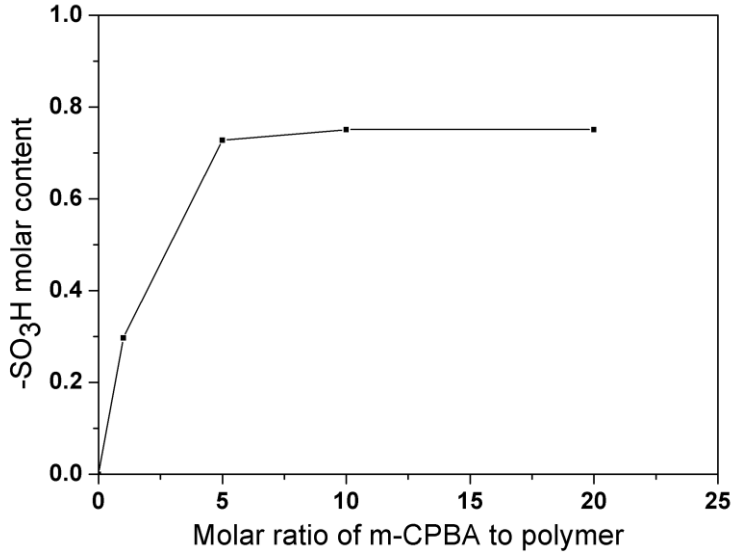

Figure S2. Molar content of –SO_3H group versus molar ratio of m-CPBA to polymer (reaction time=24 h).

References:

[1] Liautard, V.; Robert, F.; Landais, Y. *Org. Lett.* **2011**, 13, 2658-2661.