Living/controlled free radical copolymerization of chlorotrifluoroethene and butyl vinyl ether under ^{60}Co γ-ray irradiation in the presence of S-benzyl O-ethyl dithiocarbonate

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Materials:

Chlorotrifluoroethylene (CTFE) was purchased from Zhejiang Juhua Co., Ltd, China. Butyl vinyl ether (BVE) was obtained from Hubei Xinjing New Material Co., Ltd, China, 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, subsequently distilled under vacuum, and kept in a refrigerator. 2,2'-Azo-bis-isobutyronitrile (AIBN) was recrystallized from methanol twice. Acetonitrile was dried over $CaH_{2,}$ distilled, and stored in refrigerator prior to use. S-benzyl O-ethyl dithiocarbonate (BEDTC) was synthesized according to the literature.[1] All other chemicals were used as received unless otherwise noted.

Polymerization

The polymerization was performed under ^{60}Co γ-ray irradiation (20 Gy/min) at room temperature in autoclave, equipped with a manometer and control valve. First, the mixture of BVE, BEDTC and acetonitrile ([BVE] =1.1 mol/L, [BEDTC] =0.011 mol/L) was added in autoclave, and then the autoclave was immersed in liquid nitrogen for 15 min. After it was degassed by several cycles of vacuum-nitrogen, the required quantity of CTFE (the molar ratio between CTFE and BVE is 1/1.1) was introduced in the autoclave by double weighing (the difference of weight before and after transferring the CTFE into the autoclave). Finally, the autoclave was sealed by closing the control valve, and placed in an insulated room with a ^{60}Co source. The autoclave was cooled in the ice-water bath after irradiation for a prescribed time, and the unreacted CTFE gas was released slowly. The polymer was obtained by removing the solvent, and subsequently purified by precipitation in methanol. This step was repeated three times to remove the unreacted monomer. The polymer was dried under reduced pressure at 50 ^{o}C until a constant weight was attained.

The synthesis of block copolymer (P(CTFE-alt-BVE)-b-PVAc) followed the typical process: P(CTFE-alt-BVE), AIBN and vinyl acetate were added into the polymerization tube, and then the tube was degassed by three cycles of freeze-vacuum-thaw and sealed by flame under vacuum. The tube was placed in an oil bath warmed at 80 ^{o}C for 8 h. After stopping the polymerization, the mixture was diluted with THF and the solution was precipitated into methanol. The block copolymer was obtained by filtrating, reprecipitating into ethanol two more times, and drying under vacuum.

Characterization

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker DPX-400 spectrometer, using $CDCl_3$ as solvent. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured on a gel permeation chromatography (GPC) on a Waters 150C instrument equipped with 10^3-, 10^4-, and 10^5-Å Waters Ultrastyragel columns and using THF (1.0 ml/min) as the eluent. Calibration was conducted with polystyrene standards.

The theoretical molecular weights ($M_{n,th}$) are calculated according to equation (1)

$$M_{n,th}=([BVE]_0/[BEDTC]_0)\times conversion\times(\boldsymbol{M}_{BVE}+\boldsymbol{M}_{CTFE})+\boldsymbol{M}_{BEDTC} \qquad (1)$$

Where $[BVE]_0/[BEDTC]_0$ is the initial molar ratio of BVE to BEDTC, M_{BVE}, M_{CTFE} and M_{BEDTC} stand for the molecular weight of BVE, CTFE and BEDTC respectively.

The molecular weights of P(CTFE-alt-BVE) from ^{1}H NMR are calculated by equation (2)

$$M_{n,\,NMR}=(\boldsymbol{I}_{3.76}/\boldsymbol{I}_{7.35})\times 2.5\times(\boldsymbol{M}_{CTFE}+\boldsymbol{M}_{BVE})+\boldsymbol{M}_{BEDTC} \qquad (2)$$

Where $\boldsymbol{I}_{3.76}$ and $\boldsymbol{I}_{7.35}$ are the integral values of signals centered at 3.76 and 7.35 ppm, respectively. M_{BVE}, M_{CTFE} and M_{BEDTC} stand for the molecular weight of BVE, CTFE and BEDTC respectively.

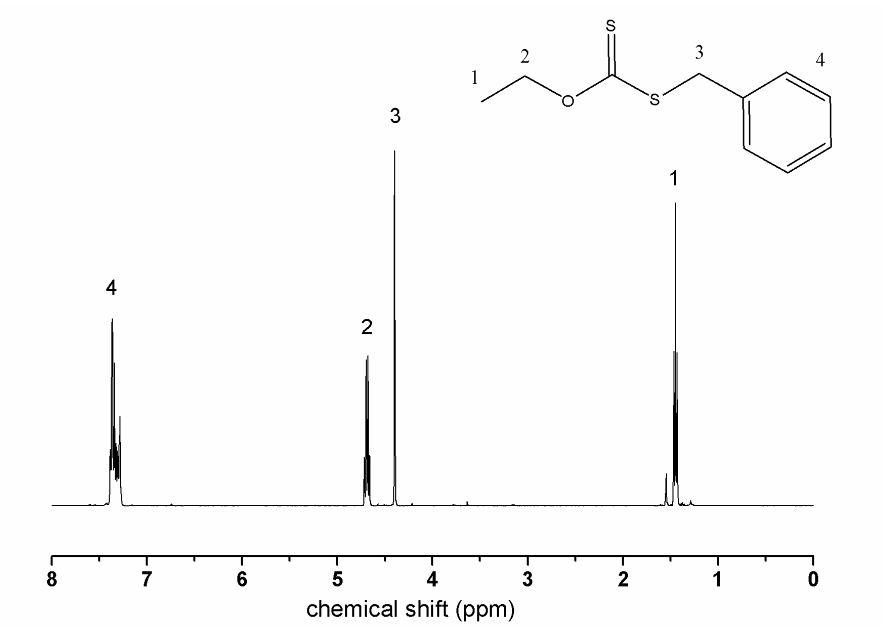

Figure S1. ^{1}H NMR spectrum of BEDTC

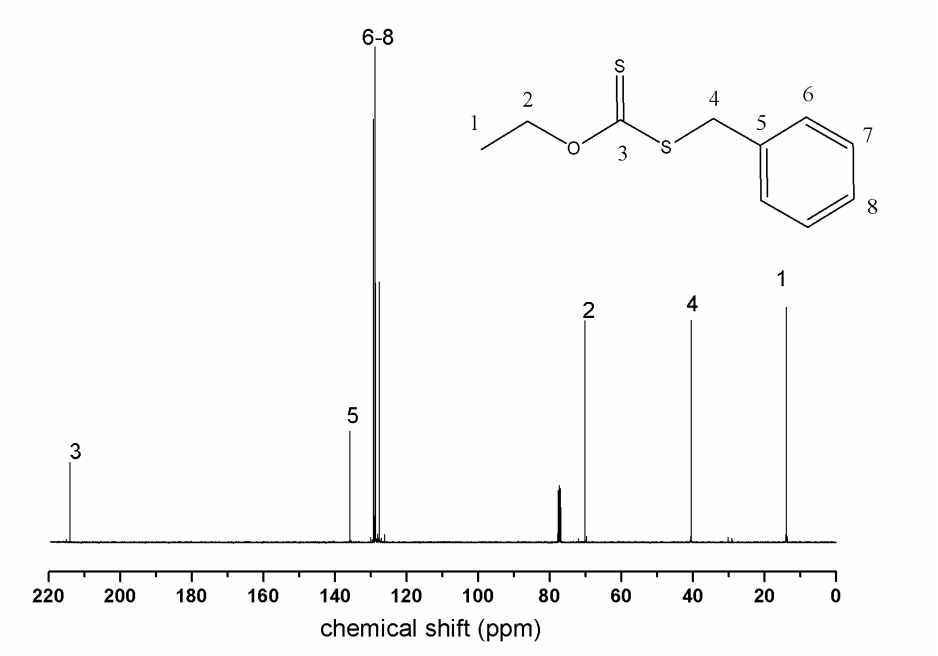

Figure S2. ^{13}C NMR spectrum of BEDTC

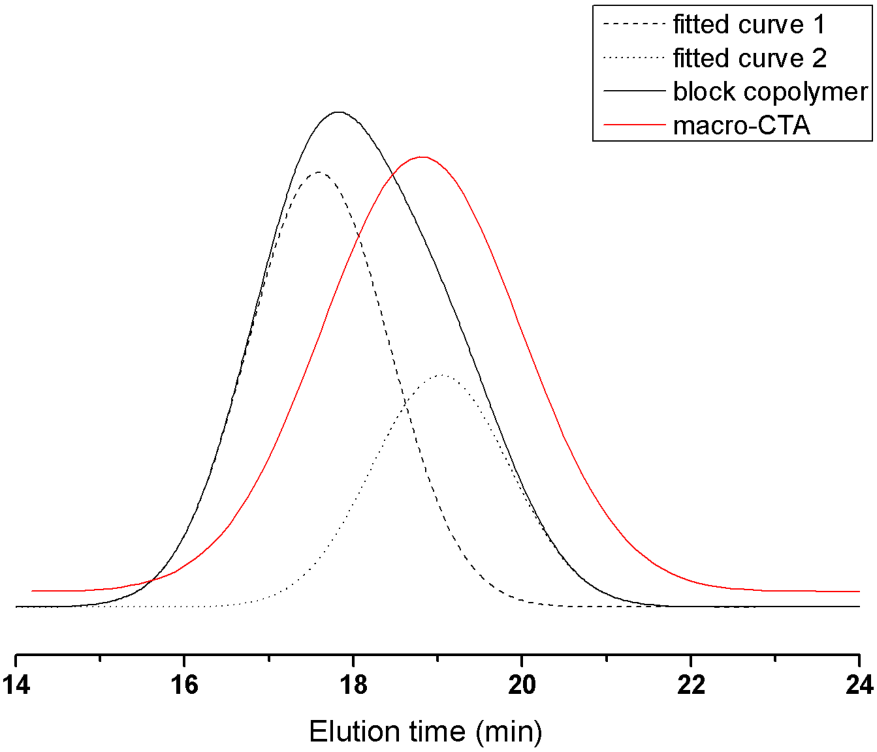

Figure S3 GPC curves of sample 4, block copolymer and deconvolution curves of the block copolymer

As we all known, the loss of some end group functionalities will increase with the increase of monomer conversion in the living/controlled free radical polymerization. Deconvolution of the molecular weight distribution of the block copolymer in GPC curve is often used to evaluate the percentage of living chains in the polymer, and the block efficiency is different due to the difference of polymerization system [2-4].

In order to evacuate chain extension polymerization in our system, we attempted the chain extension using poly(CTFE-alt-BVE) (Sample 4) as a macro-CTA. The molecular weight distribution of the block copolymer is 1.36, and the mathematical deconvolution GPC curve of the block polymer is shown in Figure S3. The red solid curve is referred to the GPC curve of macro-CTA, while the black solid curve is referred to the GPC curve of the block polymer after chain extension, which is fitted to two Gaussian distributions, and the correlation between the experimental and the theoretical curves obtained by deconvolution is 0.9972. The fitted curve 1 and 2 are corresponded to the block copolymer and macro-CTA, respectively, and the area ratio of fitted curve 1 and 2 is about 1.92:1. The percentage of living chains in the polymer can be calculated according to the reference [2].

Reference:

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