SUPPORTING INFORMATION

Facile Preparation of Stereochemistry-controllable Biobased Poly(butylene maleate-co-butylene fumarate) Unsaturated Copolyesters: A Chemoselective Polymer Platform for Versatile Functionalization via Aza-Michael Addition

Yang Yu, Zhiyong Wei*, Xuefei Leng, Yang Li

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

* Corresponding author

Email address: zywei@dlut.edu.cn (Z. Wei)

Calculation of average sequence length of butylene maleate (L_{ncis}) and butylene fumarate (L_{ntrans}) segments, and the degree of polyester randomness (R). The resonance absorptions of the α-carbon of butylene segment were resolved with a curve-fitting program based on the least squares parameter adjustment criterion using the Gauss-Newton iteration procedure. The fitting process adjusts the peak position, the curve shape (a Gaussian fraction; whereby zero represents a pure Lorentzian and unity represents a pure Gaussian), and the peak width and the height in such a way that a best fit is obtained. The excellent agreement between the experimental and fitted spectra were founded with a regression coefficient R^2>0.995, Figure S1 displayed the resolution result of Entry 12, as an instance. The four triads are assigned to fumarate butylene maleate (*trans*/*cis*) at 64.75 ppm, fumarate butylene fumarate (*trans*/*trans*) at 64.70 ppm, maleate butylene maleate (*cis*/*cis*) at 64.62 ppm, and maleate butylene fumarate (*cis*/*trans*) at 64.56 ppm, respectively. From the four peak areas ($A_{trans/cis}$, $A_{trans/trans}$, $A_{cis/cis}$, and $A_{cis/trans}$), molar ratios of butylene fumarate (P_{trans}) and butylene maleate (P_{cis}) groups were firstly calculated by the following equations:

$$P_{trans} = [(A_{trans/cis} + A_{cis/trans})/2 + (A_{trans/trans})]$$

$$P_{cis} = [(A_{trans/cis} + A_{cis/trans})/2 + (A_{cis/cis})]$$

Next, the following equations were used to calculate number average sequence length of butylene maleate (L_{ncis}) and butylene fumarate (L_{ntrans}) segments:

$$L_{ntrans} = 2\ P_{trans} / (\ A_{trans/cis} + A_{cis/trans})$$

$$L_{ncis} = 2\ P_{cis} / (\ A_{trans/cis} + A_{cis/trans})$$

Then, the following equation was used to calculate the degree of randomness (R):

$$R = 1/\ L_{ntrans} + 1/\ L_{ncis}$$

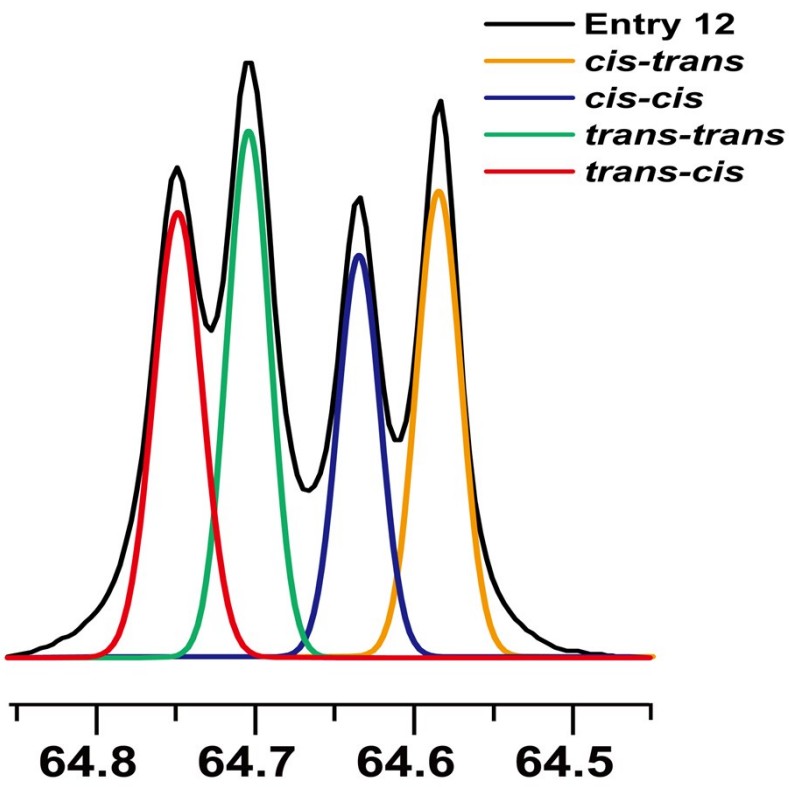

Figure S1. Peak fitting of the methylene carbon resonance in quantitative ^{13}C NMR spectrum of Entry12 as an example.

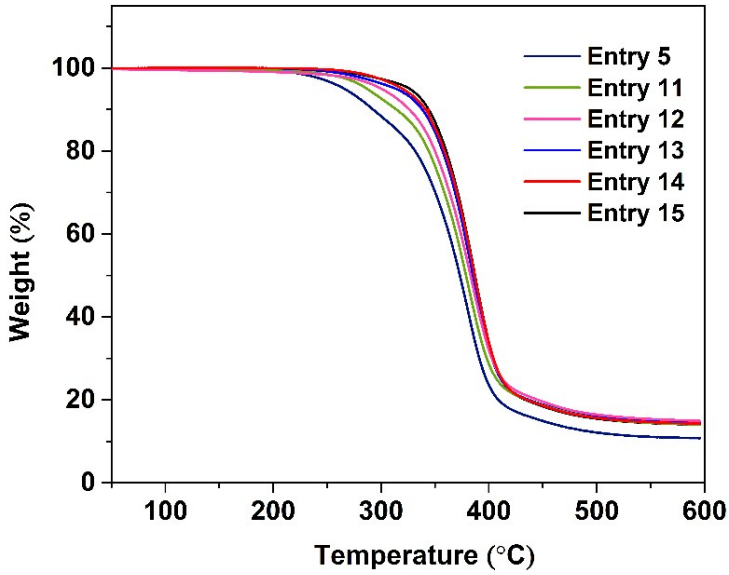

Figure S2. Thermoanalytical curves of poly(BM-co-BF) copolyesters.

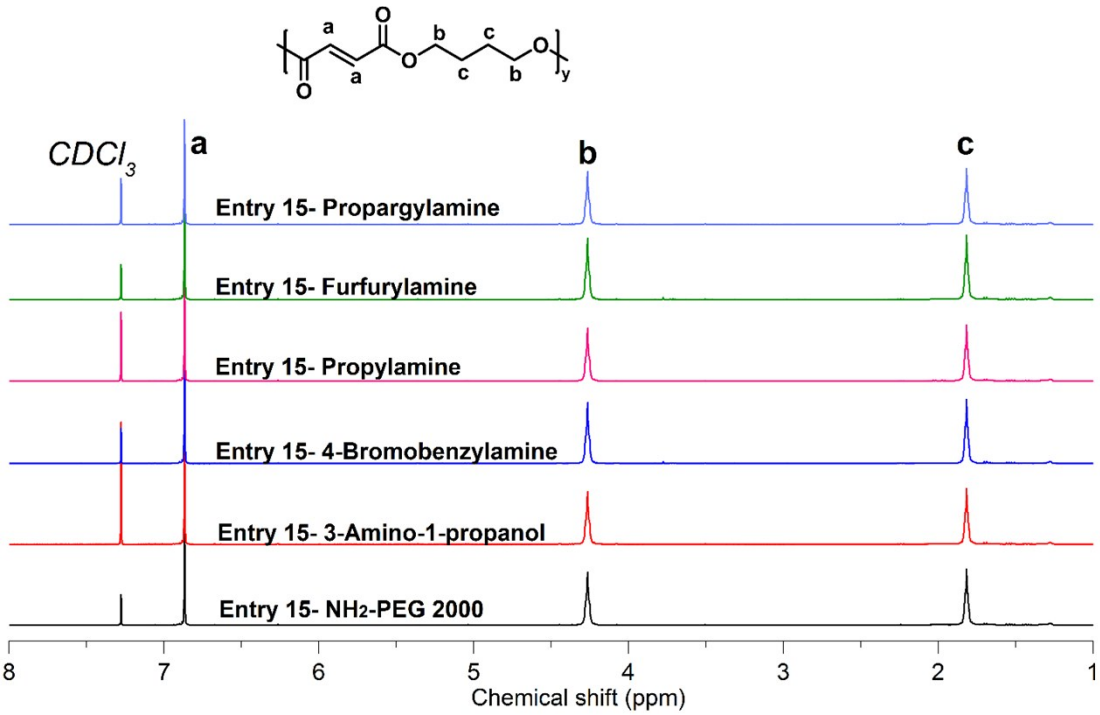

Figure S3. ^{1}H NMR spectra of model reaction. Entry 15 reacted with primary amine compounds for 10h at room temperature, and no aza- Michael addition occurred.

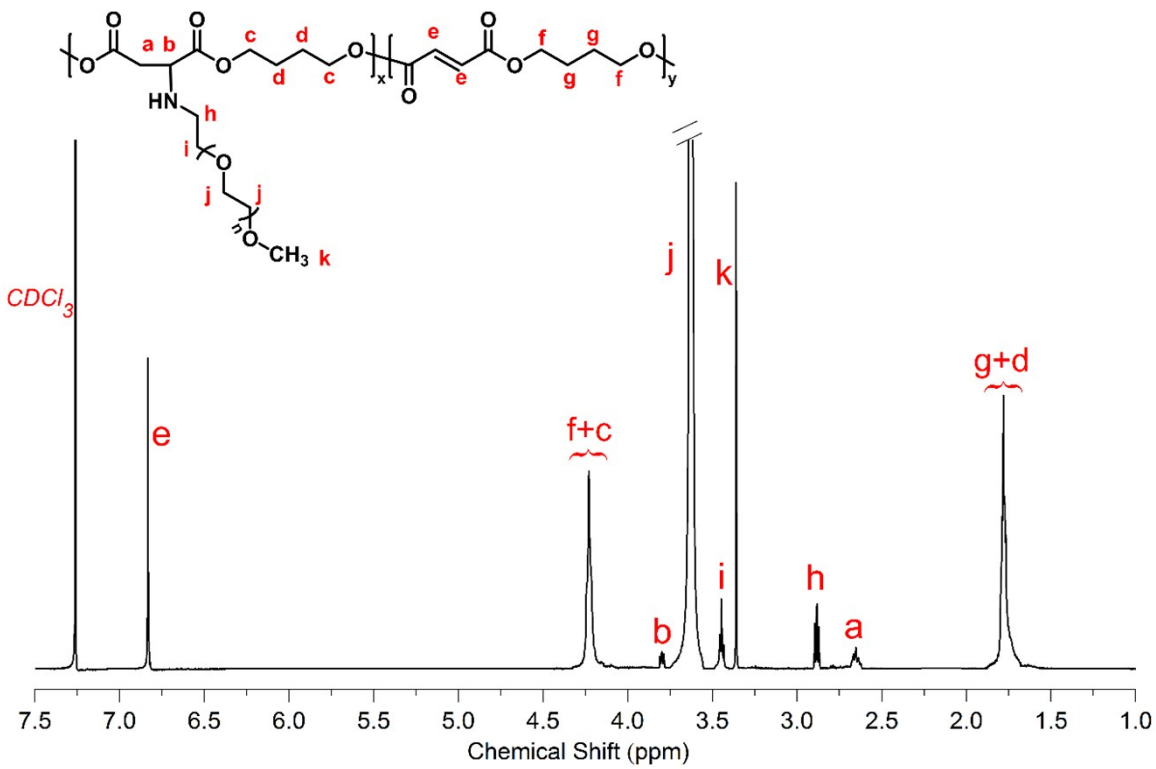

Figure S4. [1]H NMR spectrum of Entry 16 prepared by Michael addition of Entry5 with NH_2-PEG 2000.

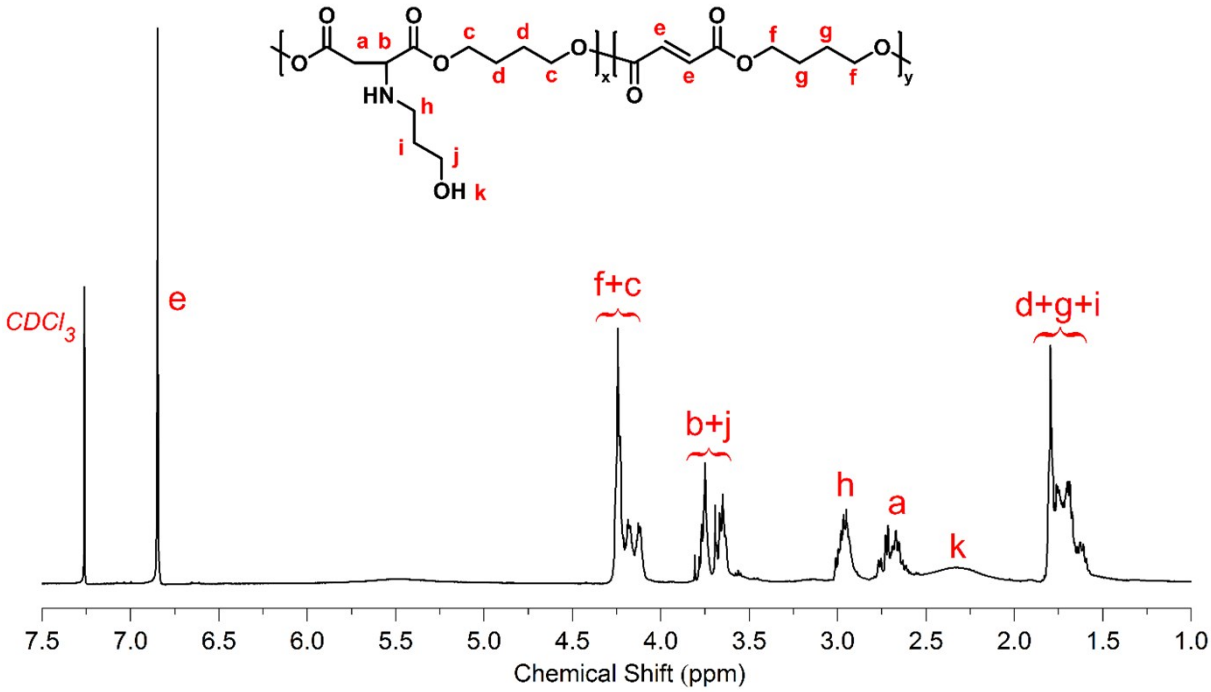

Figure S5. [1]H NMR spectrum of Entry 17 prepared by Michael addition of Entry5 with 3-Amino-1-propanol.

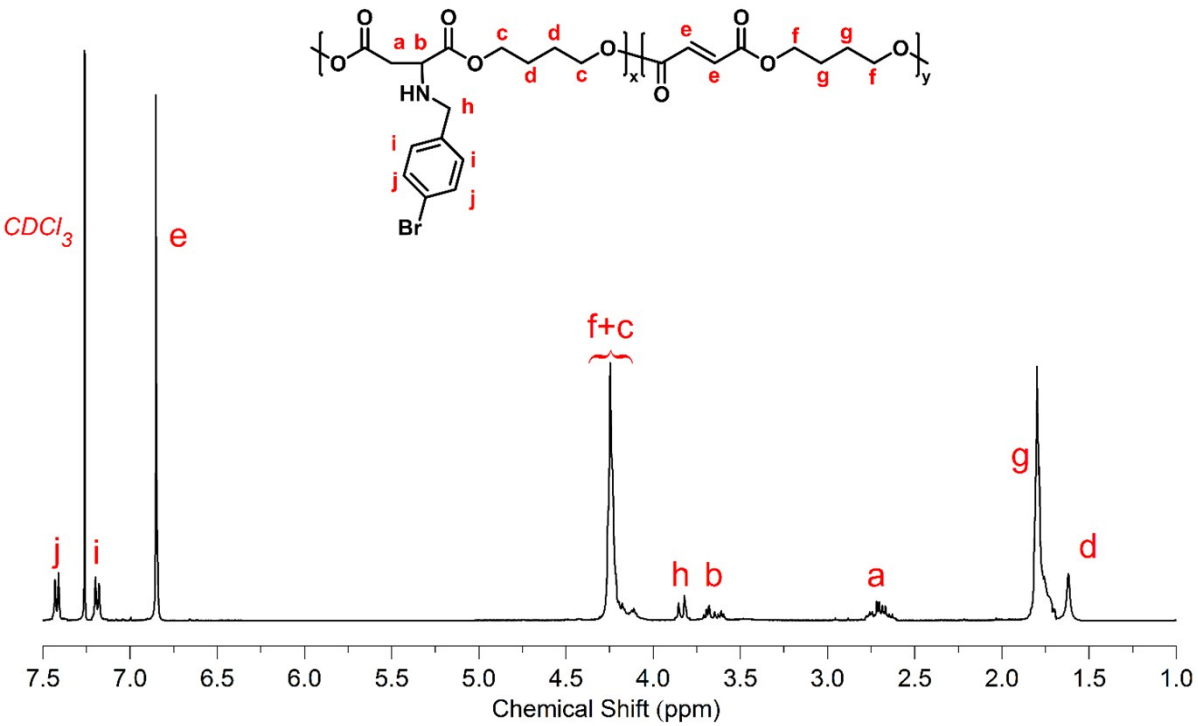

Figure S6. [1]H NMR spectrum of Entry 18 prepared by Michael addition of Entry5 with 4-Bromobenzylamine.

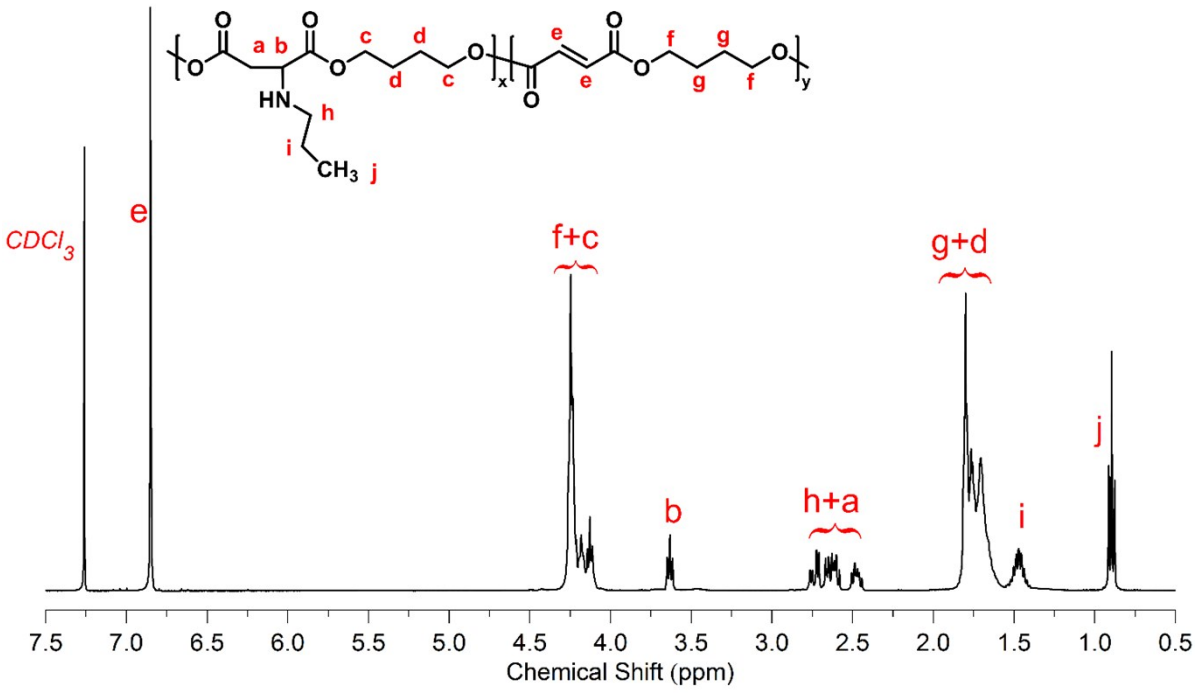

Figure S7. [1]H NMR spectrum of Entry 19 prepared by Michael addition of Entry5 with propylamine.

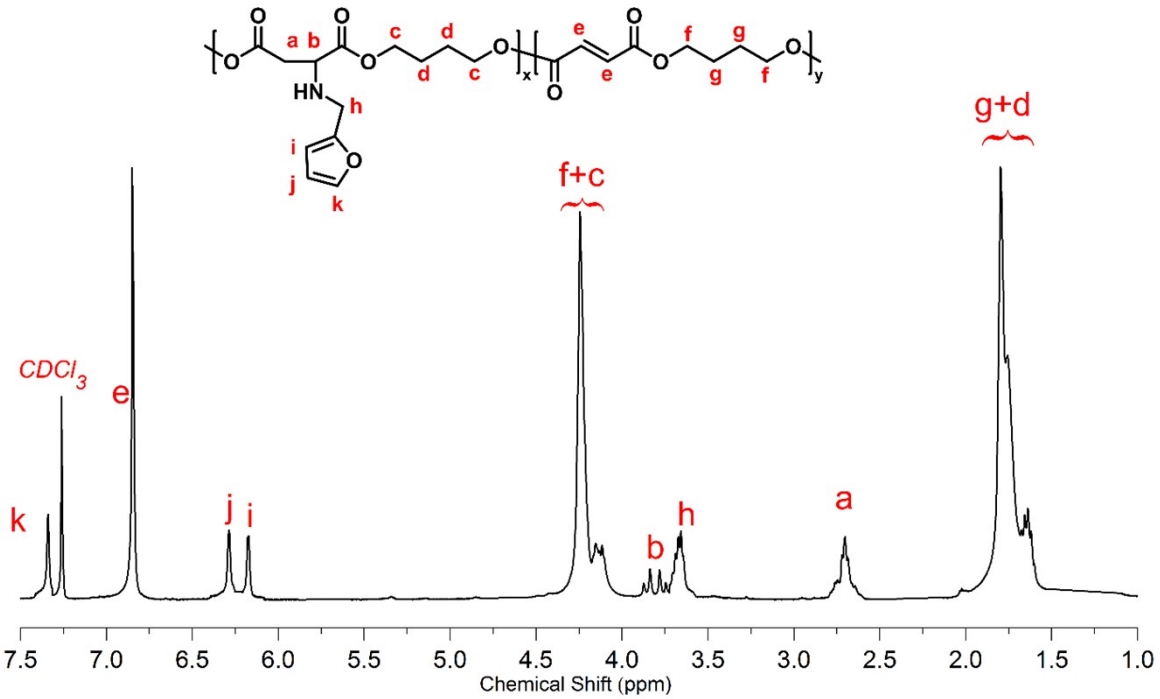

Figure S8. [1]H NMR spectrum of Entry 20 prepared by Michael addition of Entry5 with furfurylamine.

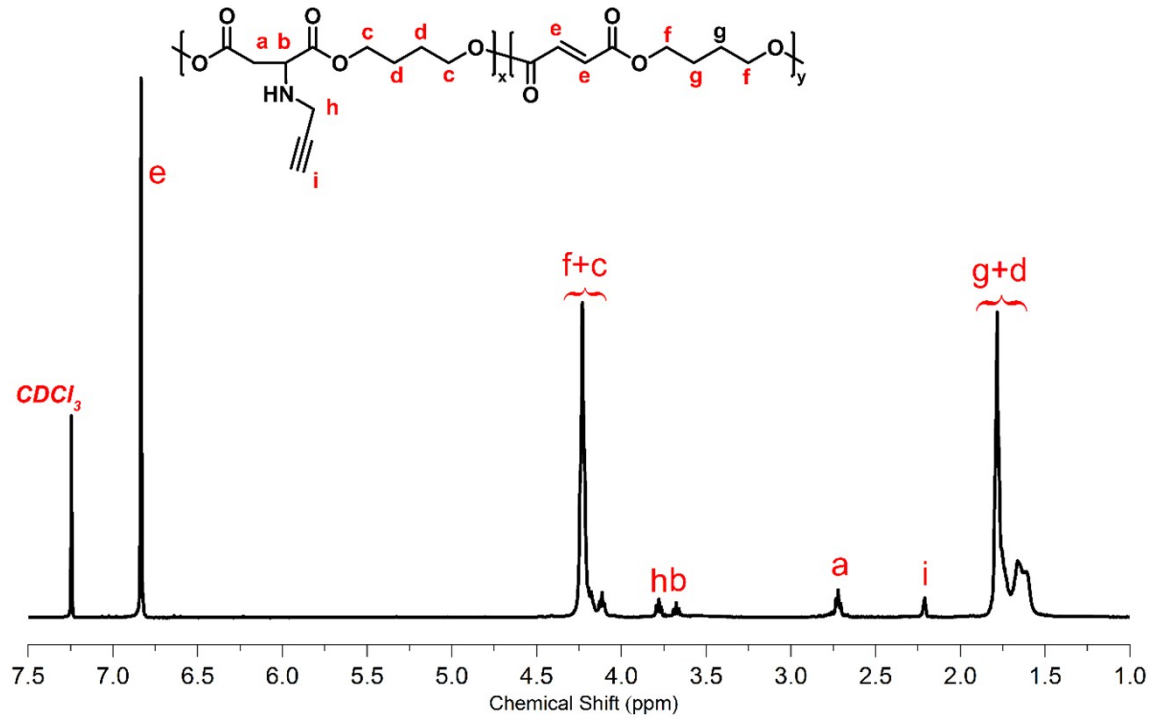

Figure S9. [1]H NMR spectrum of Entry 21 prepared by Michael addition of Entry5 with propargylamine.

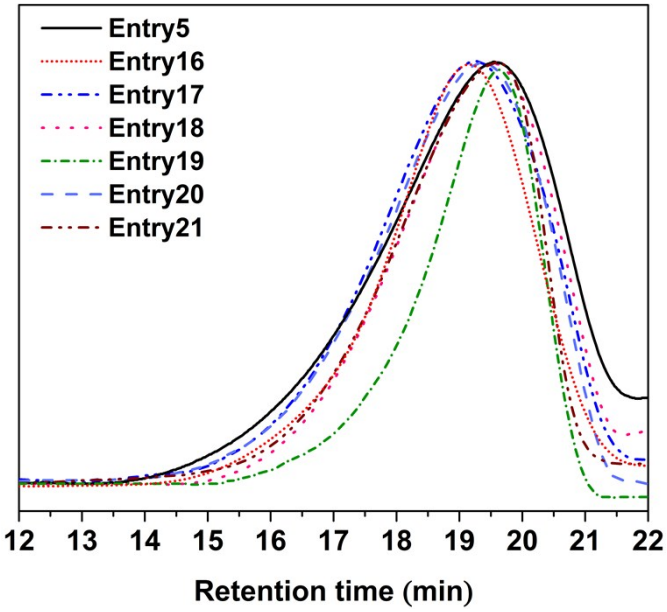

Figure S10. GPC curves of Entries 5, 16-21.