Electronic Supplementary Information

Synthesis of alkynyl-functional linear and star polyethers by aluminium-catalyzed copolymerization of glycidyl 3-butynyl ether with ethylene oxide and epichlorohydrin

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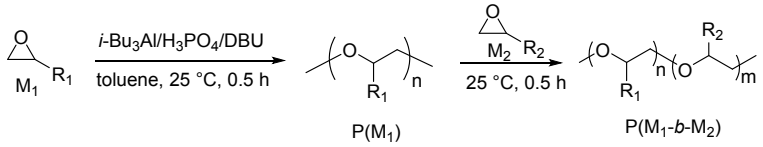
Content

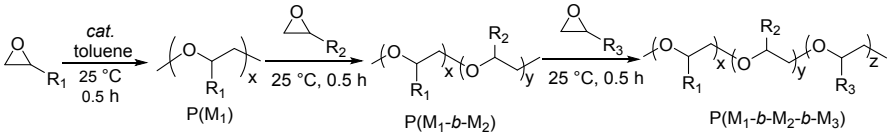
Table S1 Detail information of the obtained diblock copolymers via *i*-Bu_3Al/H_3PO_4/DBU[a].



run	Monomer (M_1/M_2))	Monomer feed (mmol)	P(M_1)		P(M_1-*b*-M_2)					
			M_n[b] (×10^4)	PDI[b]	Yield (%)	M_1 (mol%)	M_n[b] (×10^4)	PDI[b]	T_g[c] (ºC)	T_m[c] (ºC)
Table 1, run 5	GBE-EO	2/8	3.0	1.36	>99	18	6.8	1.45	-41	61
Table 1, run 6	GBE-ECH	12/8	10.2	1.37	>99	57	18.9	1.35	-41/-26	-
Table 1, run 7	EO-GBE	4/6	1.6	1.23	>99	39	8.2	1.46	-41	53
Table 1, run 8	ECH-GBE	4/6	3.3	1.35	>99	43	9.3	1.35	-41/-26	-

[a] Reaction condition: *i*-Bu_3Al/H_3PO_4/DBU molar ratio was 1/0.33/0.25, *i*-Bu_3Al = 0.25 mmol; monomer concentration, 2 mol/L in toluene; [b] Determined by GPC in 1,2,4-trichlorobenzene at 150 ºC against polystyrene standard. [c] Determined by DSC.

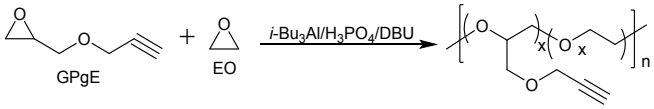
Table S2 Detail information of the obtained triblock copolymers via *i*-Bu_3Al/H_3PO_4/DBU[a].



run	Monomer ($M_1/M_2/M_3$)	Monomer feed (mmol)	P(M_1)		P(M_1-*b*-M_2)			P(M_1-*b*-M_2-*b*-M_3)			
			M_n[b] (×10^4)	PDI[b]	*Composition*[d] M_1/M_2(mol%)	M_n[b] (×10^4)	PDI[b]	Yield %	*Composition* $M_1/M_2/M_3$ (mol%)	M_n[b] (×10^4)	PDI[b]
Table 1 run 9	GBE/ECH/EO	2/4/4	3.0	1.36	33/67	7.3	1.42	>99	20/40/40	9.1	1.56
Table 1 run 10	GBE/ECH/EO	2/4/14	3.0	1.36	33/67	7.3	1.42	>99	10/20/70	14.3	1.58
Table 1 run 11	ECH/GBE/EO	4/2/4	4.3	1.38	67/33	7.2	1.42	>99	40/20/40	9.1	1.53

[a] Reaction condition: *i*-Bu_3Al/H_3PO_4/DBU molar ratio was 1/0.33/0.25, *i*-Bu_3Al = 0.25 mmol; monomer concentration, 2 mol/L in toluene; [b] Determined by GPC in 1,2,4 trichlorobenzene at 150 ºC against polystyrene standard.

Table S3 Polymerization results of GPgE with ethylene oxide EO by *i*-Bu_3Al/H_3PO_4/DBU[a]



Run	Feed ratio (mmol)		Yield	Composition[b](mol%)		M_n[c] (×10^4)	M_w/M_n[c]	T_g[d] (°C)	T_m[d] (°C)
	GPgE	EO	(%)	GPgE	EO				
1	10	0	>99	100	0	10.9	1.47	-32	–
2	5.0	5.0	>99	49	51	9.7	1.44	-36	–

[a] Reaction condition: *i*-Bu_3Al/H_3PO_4/DBU molar ratio, 1/0.33/0.25; *i*-Bu_3Al 0.25 mmol; monomer concentration, 2 mol/L in toluene; 25 ºC; reaction time, 0.5 h. [b] Determined by ^{1}H-NMR. [c] Determined by GPC in 1,2,4-trichlorobenzene at 150 ºC against polystyrene standard. [d] Determined by DSC.

Table S4 Detail information of GBE polymerization versus different conversion via *i*-Bu_3Al/H_3PO_4/DBU[a].

Run	Time (min)	GBE feed ratio (mmol)	Conversion (%)	M_n[b]($\times 10^4$)	M_w/M_n[b]
1	8	20	64.3	14.1	1.44
2	30	20	100	21.2	1.46
3[c]	60	20+10	150[d]	32.4	1.47

[a] Reaction condition: *i*-Bu_3Al/H_3PO_4/DBU molar ratio, 1/0.33/0.25; *i*-Bu_3Al 0.25 mmol; monomer concentration, 2 mol/L in toluene; 25 °C. [b] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard. [c] 20 mmol GBE was first polymerized in 25 °C, 30 min, then another 10 mmol GBE was added to further polymerization. [d] Relative to the first added 20 mmol GBE.

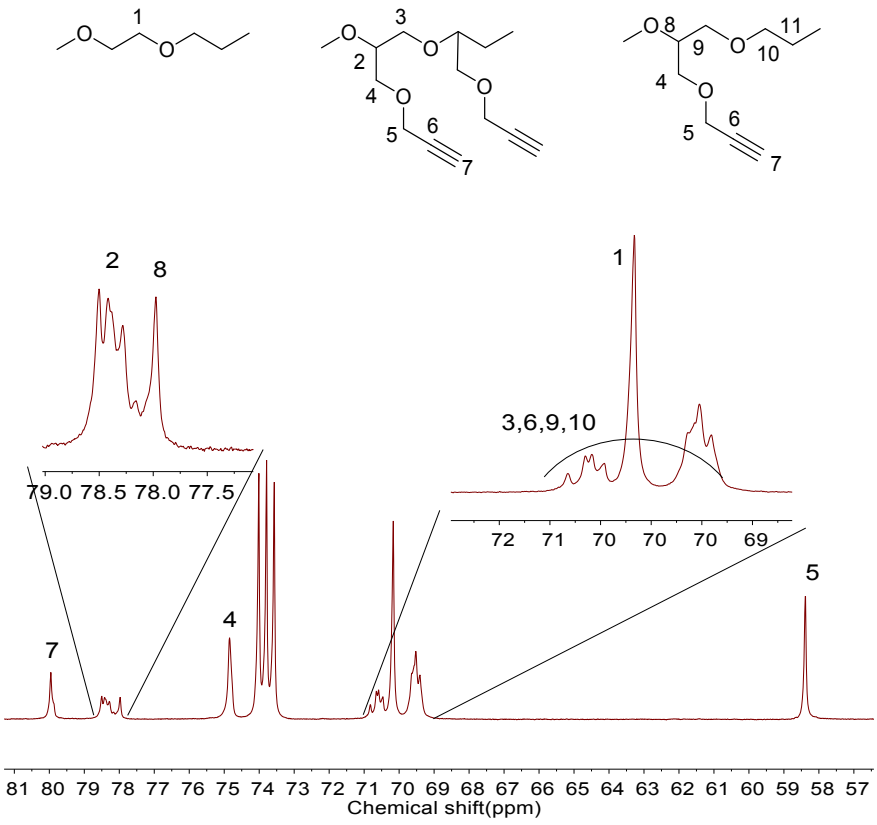


Fig. S1 ^{13}C-NMR spectrum of a GPgE-EO copolymer with 49 mol% GPgE.

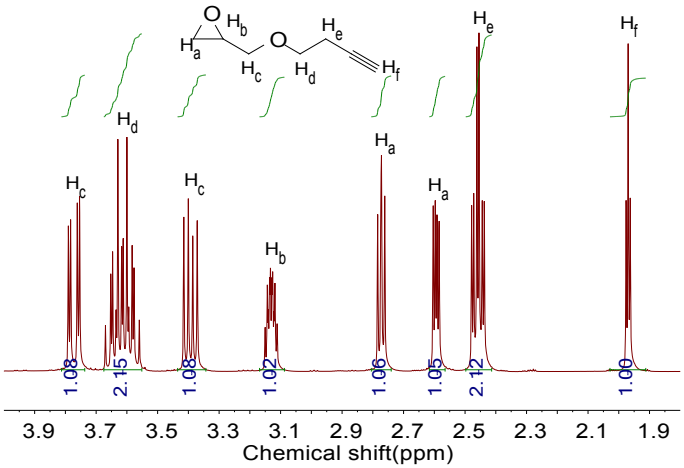


Fig. S2 ^{1}H-NMR spectrum of GBE monomer.

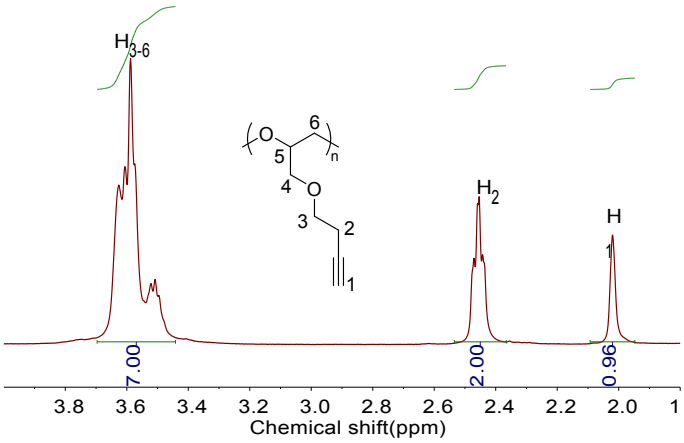


Fig. S3 ^{1}H-NMR spectrum of a GBE homopolymer.

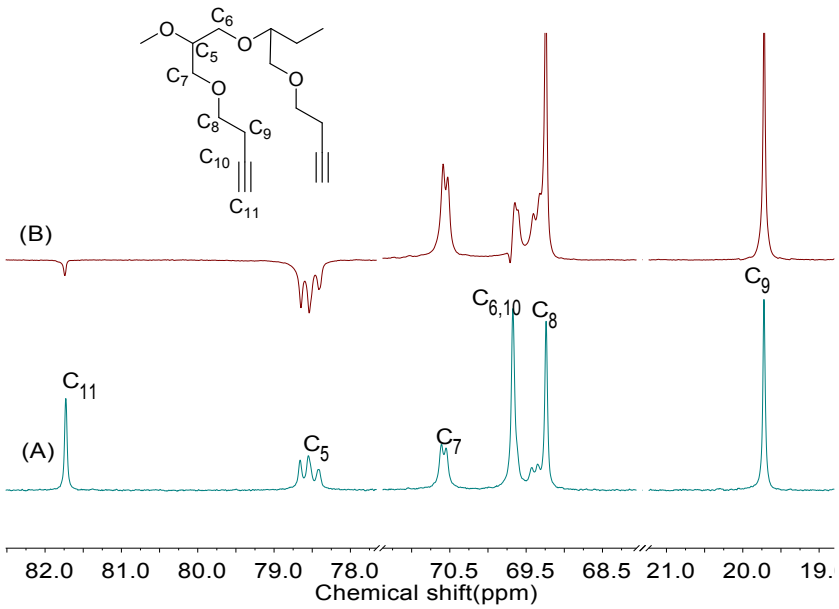


Fig. S4 DEPT-135-^{13}C-NMR spectrum of a GBE homopolymer**.**

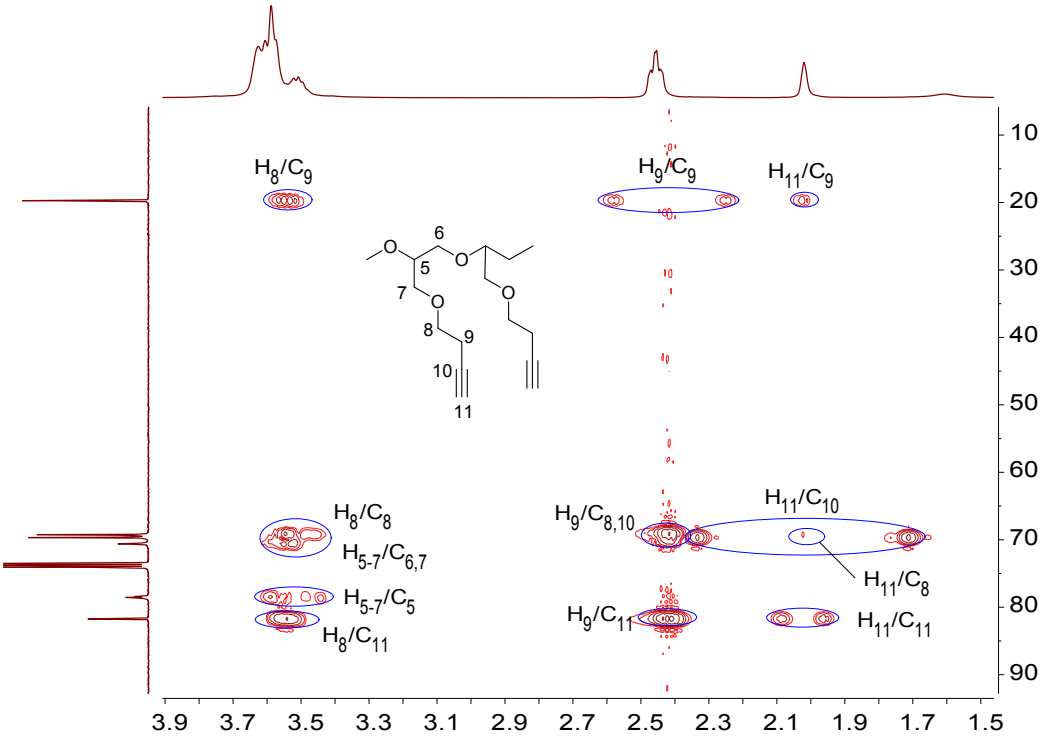


Fig. S5 HMBC NMR spectrum of a GBE homopolymer**.**

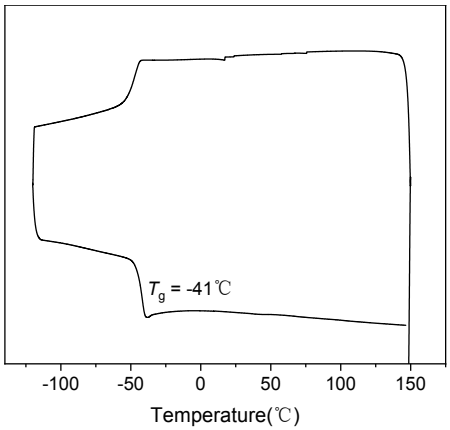


Fig. S6 DSC curve of a GBE homopolymer

r.

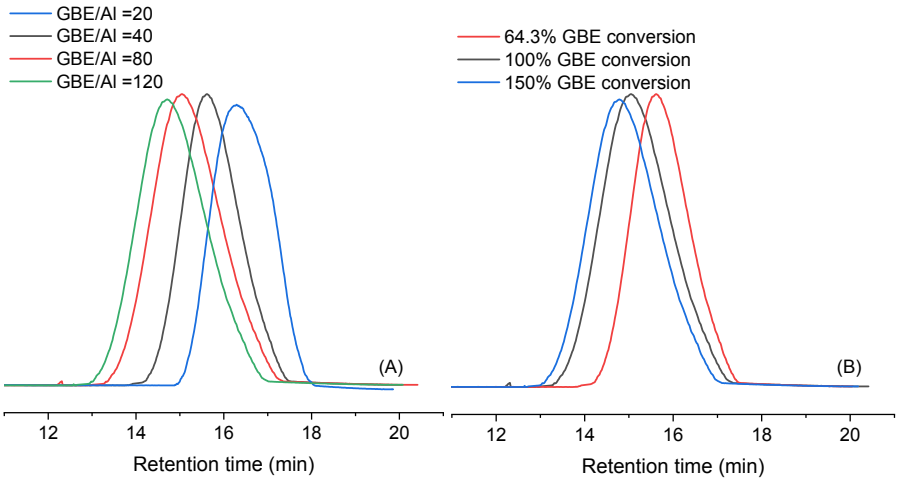


Fig. S7 GPC traces of GBE homopolymer versus GBE/Al ratio, and GBE conversion.

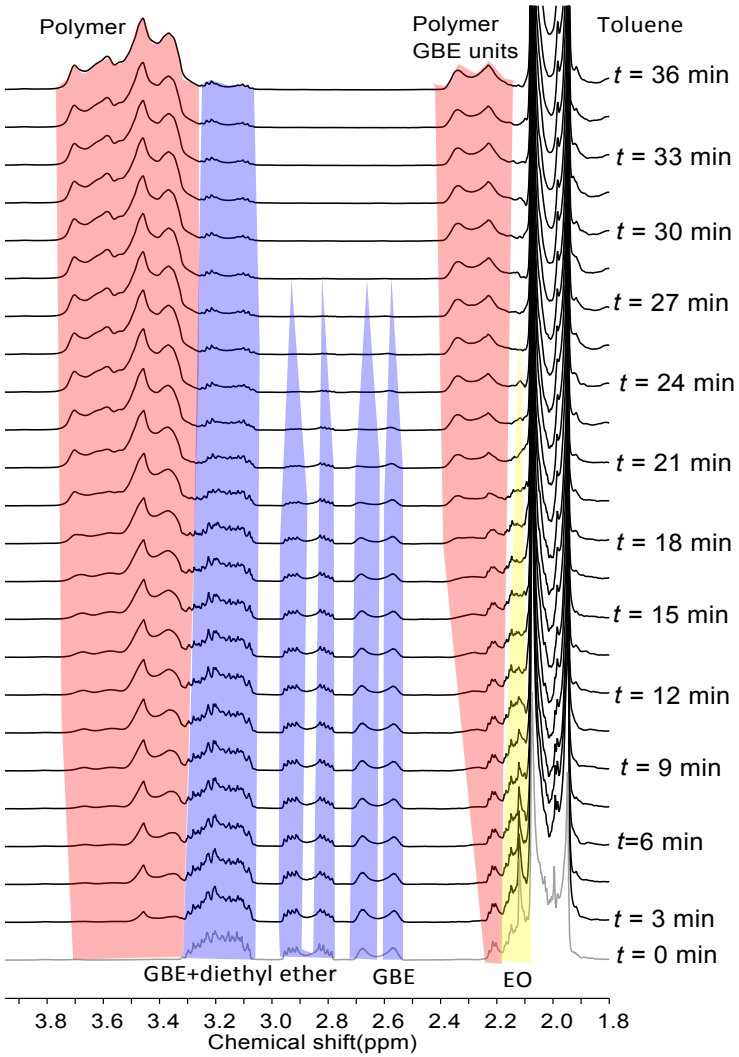


Fig. S8 ^{1}H-NMR spectra of kinetic experiment of GBE-EO copolymerization. GBE and diethyl ether were shaded in blue, EO monomer was shaded in yellow, the copolymer was shaded in red.

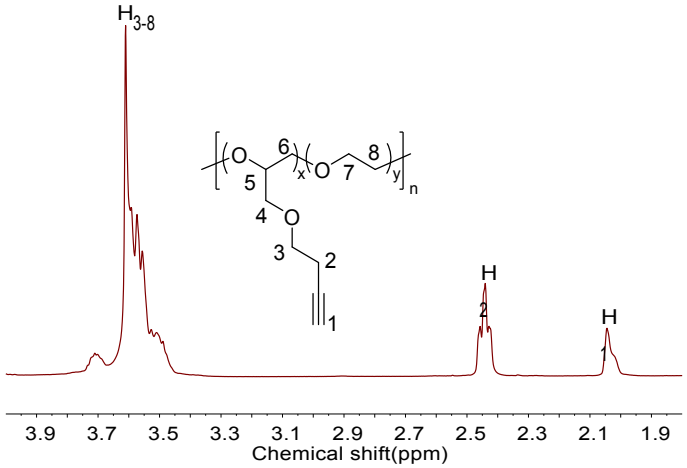


Fig. S9 ^{1}H-NMR spectrum of a GBE-EO copolymer with 51 mol% GBE by simultaneous copolymerization.

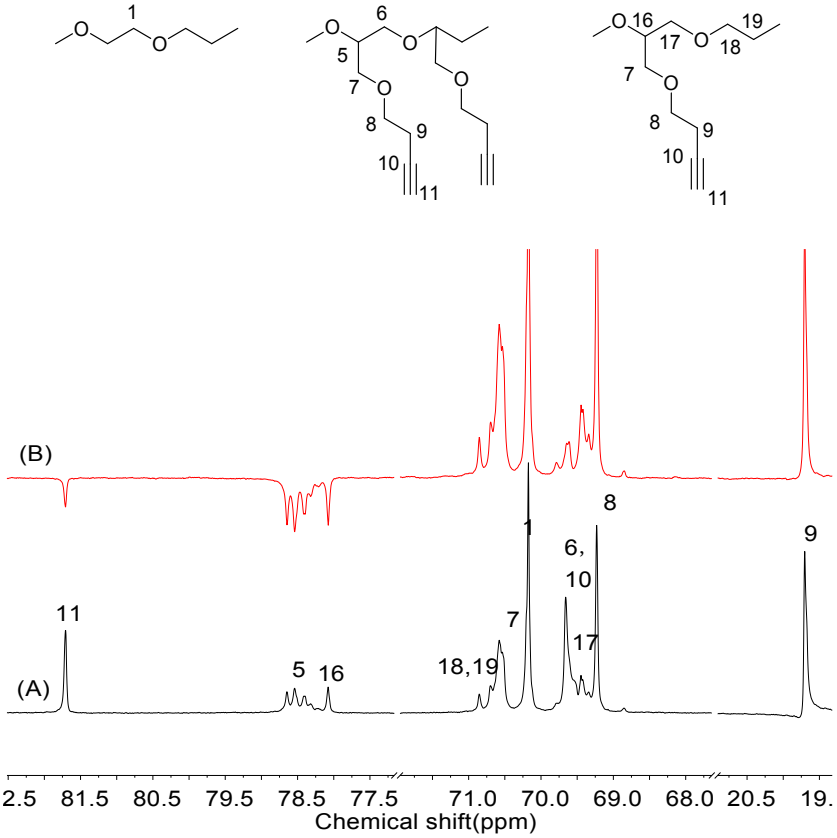


Fig. S10 DEPT-135-^{13}C-NMR spectrum of a GBE-EO copolymer with 51 mol% GBE by simultaneous copolymerization.

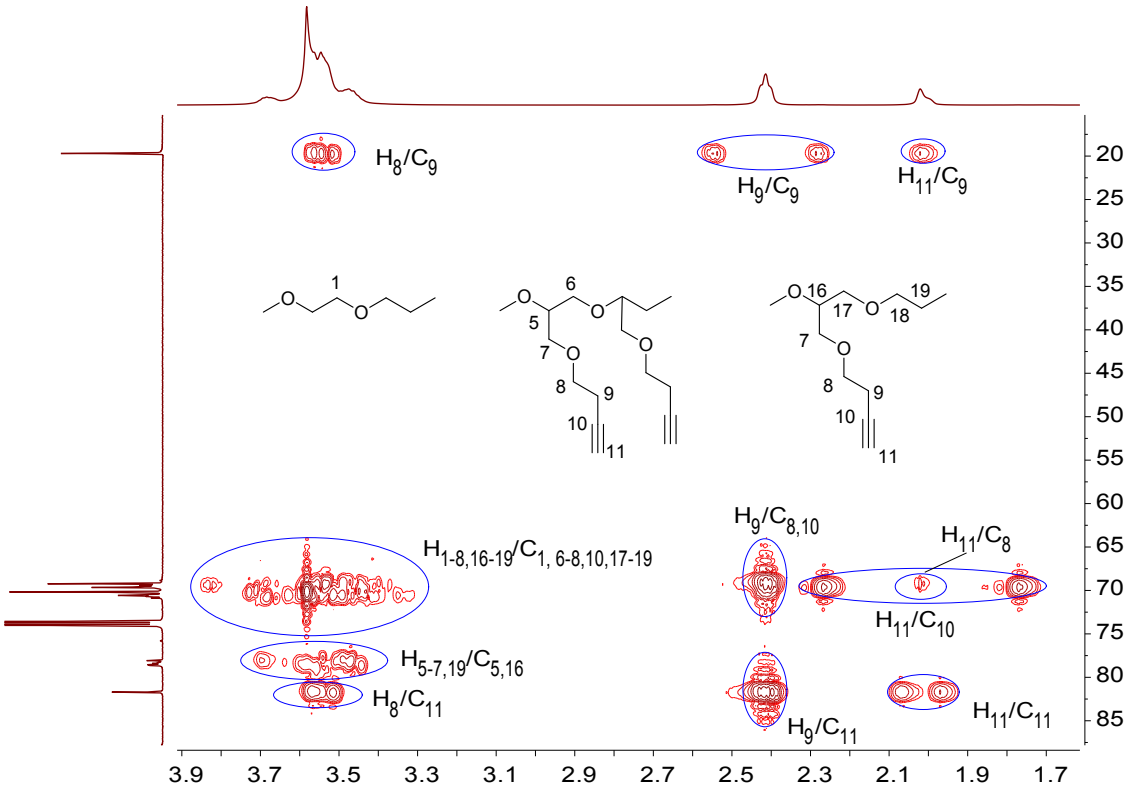


Fig. S11 HMBC NMR spectrum of a GBE-EO copolymer with 51 mol% GBE by simultaneous copolymerization.

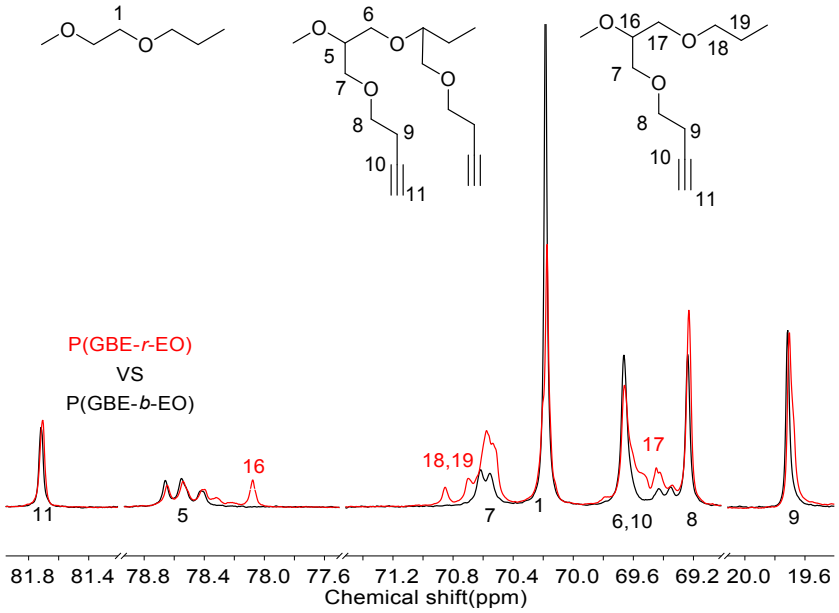


Fig. S12 ^{13}C-NMR spectra of a GBE-EO copolymer with 51 mol% GBE (Red line) by simultaneous copolymerization and a GBE-EO diblock polymers with 57 mol% GBE (Black line) by sequential copolymerization.

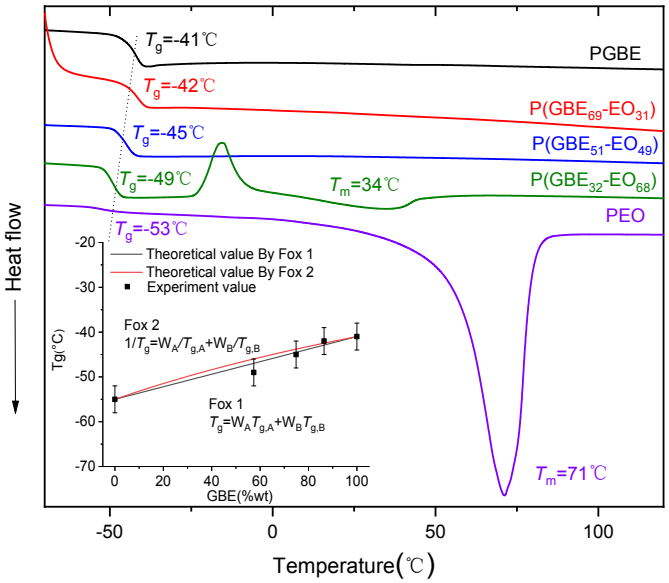


Fig. S13 DSC curves of GBE-EO copolymers with different compositions by simultaneous copolymerization.

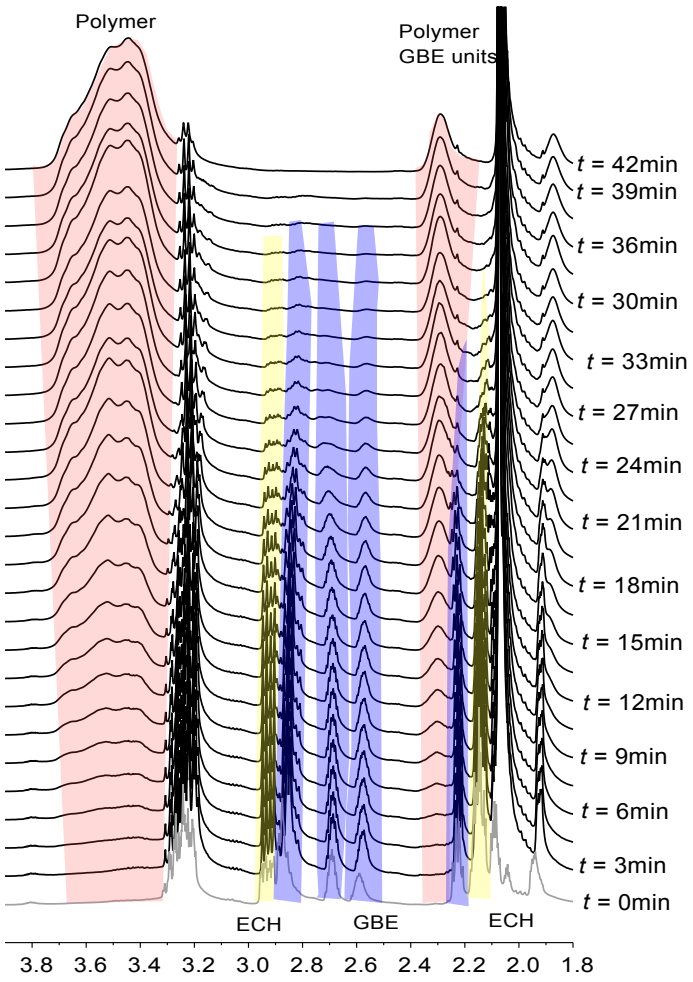


Fig. S14 ^{1}H-NMR spectra of kinetic experiment of the GBE-ECH copolymerization. GBE monomer was shaded in blue, ECH monomer was shaded in yellow, the copolymer was shaded in red.

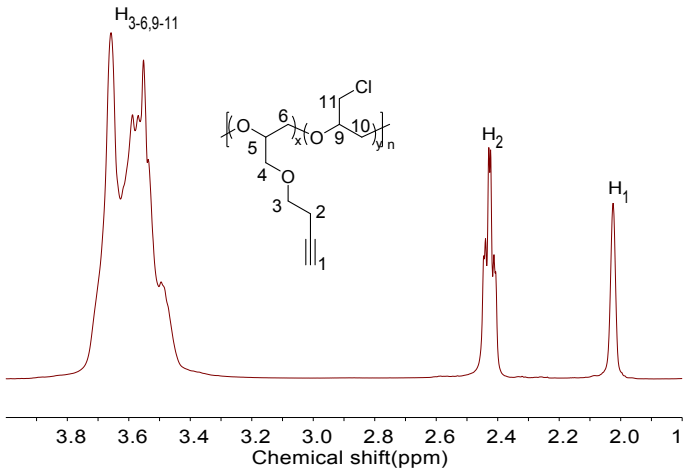


Fig. S15 ^{1}H-NMR spectrum of a GBE-ECH copolymer with 48 mol% GBE by simultaneous copolymerization.

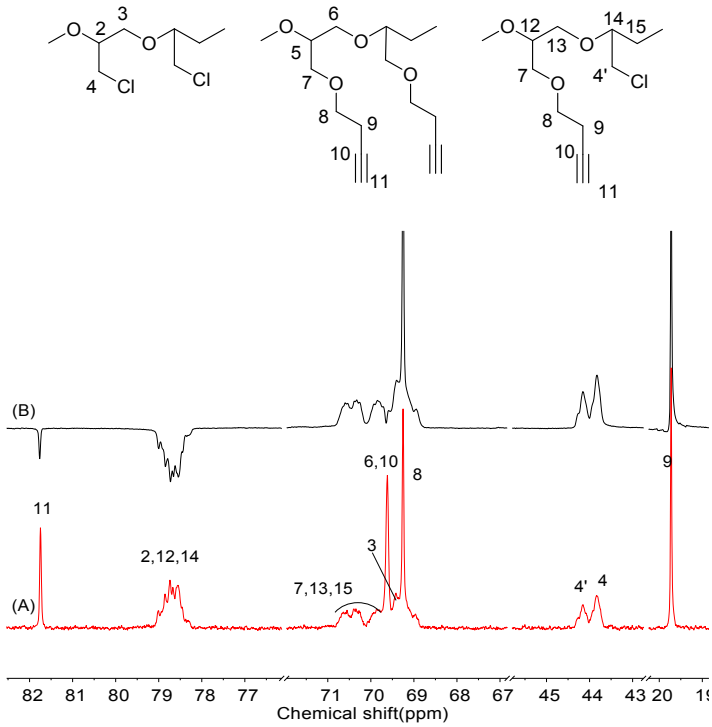


Fig. S16 DEPT-135-^{13}C-NMR spectrum of a GBE-ECH copolymer with 48 mol% GBE by simultaneous copolymerization**.**

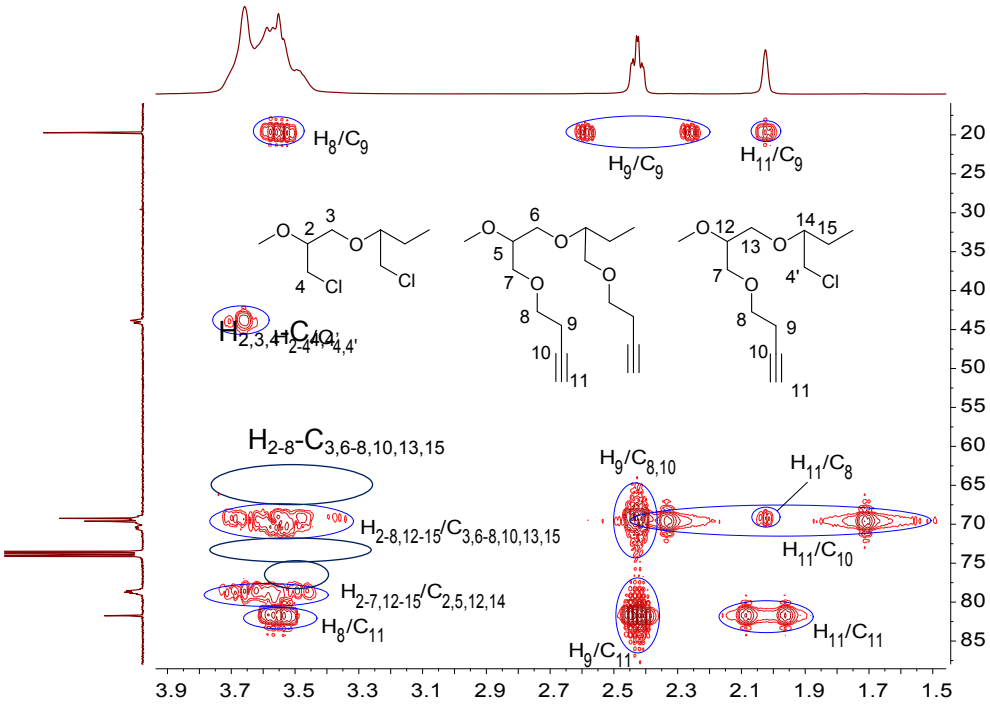


Fig. S17 HMBC NMR spectrum of a GBE-ECH copolymer with 48 mol% GBE by simultaneous copolymerization.

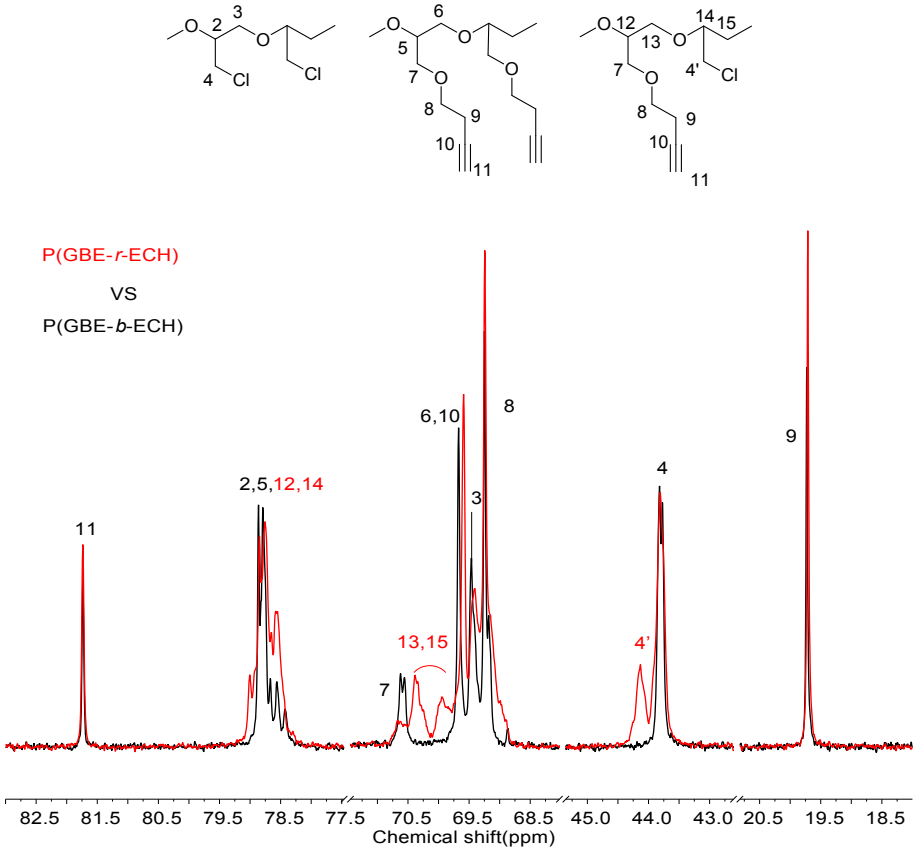


Fig. S18 ^{13}C-NMR spectra of a GBE-ECH copolymer with 29 mol% GBE (Red line) by simultaneous copolymerization and a GBE-ECH diblock copolymer with 33 mol% GBE (Black line) by sequential copolymerization.

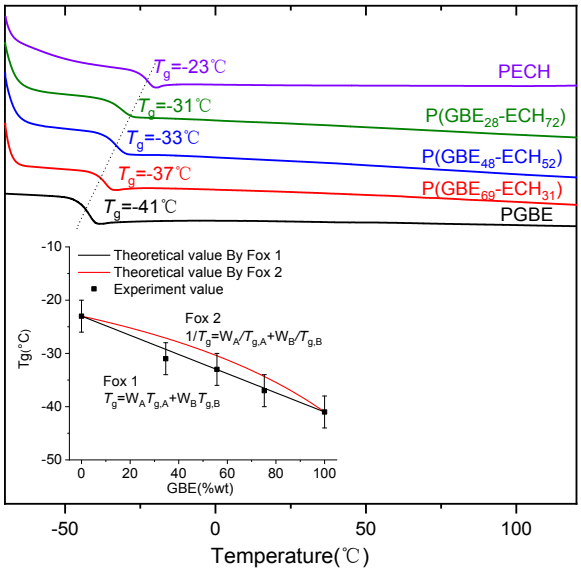


Fig. S19 DSC curves of GBE-ECH copolymers with different compositions by simultaneous copolymerization.

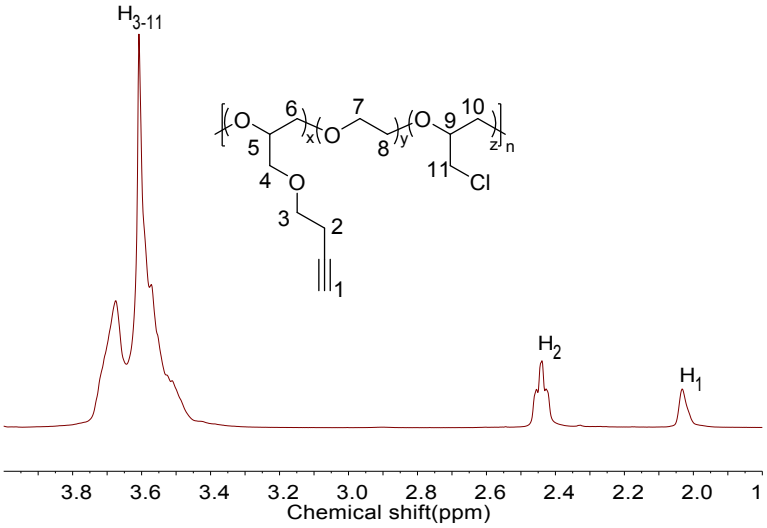


Fig. S20 ^{1}H-NMR spectrum of a GBE-EO-ECH terpolymer with 24 mol% GBE, 50 mol% EO, and 26 mol% ECH by simultaneous terpolymerization.

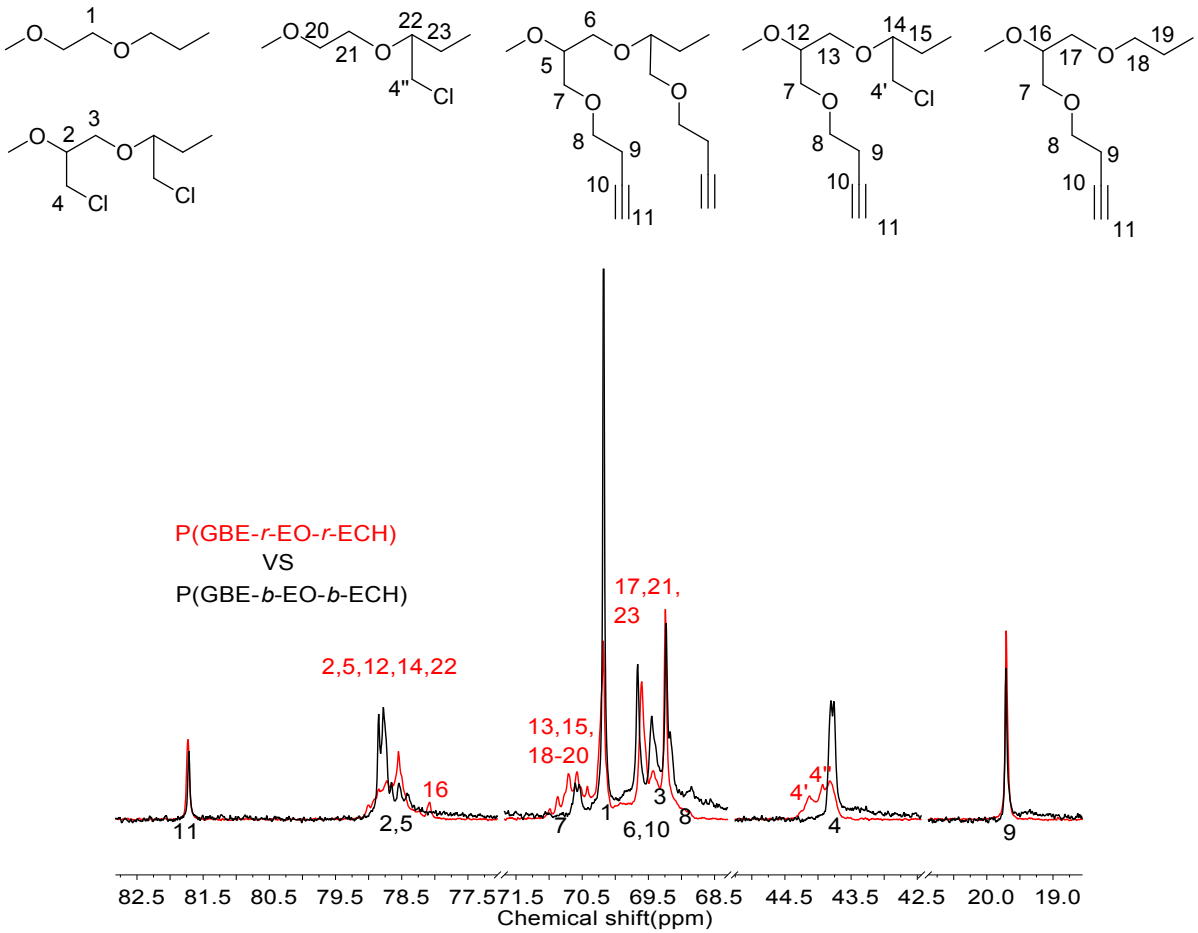


Fig. S21 ^{13}C-NMR spectra of a GBE-ECH-EO terpolymer with 30 mol% GBE, 35 mol% EO, and 35 mol% ECH (Red line) by simultaneous terpolymerization and a GBE-ECH-EO triblock copolymer with 20 mol% GBE, 40 mol% EO, and 40 mol% ECH (Black line) by sequential terpolymerization.

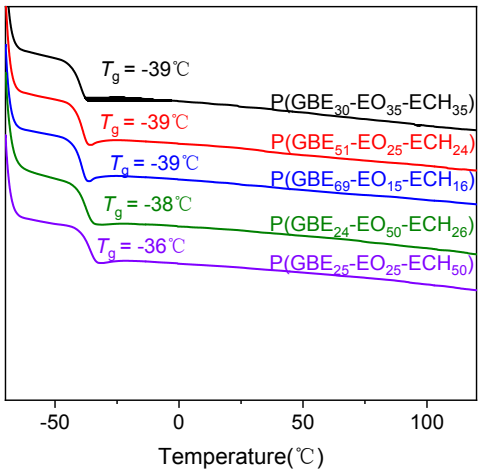


Fig. S22 DSC curves of GBE-EO-ECH terpolymers with different compositions by simultaneous terpolymerization.

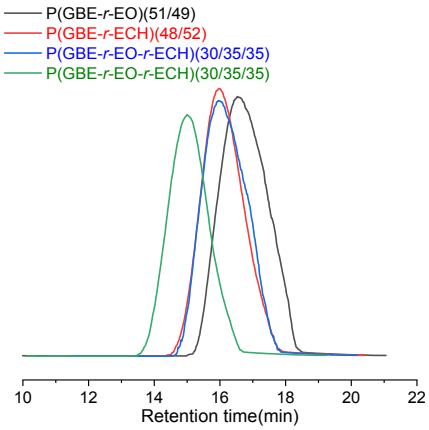


Fig. S23 GPC traces of a GBE-EO, GBE-ECH, GBE-EO-ECH copolymers by simultaneous terpolymerization.

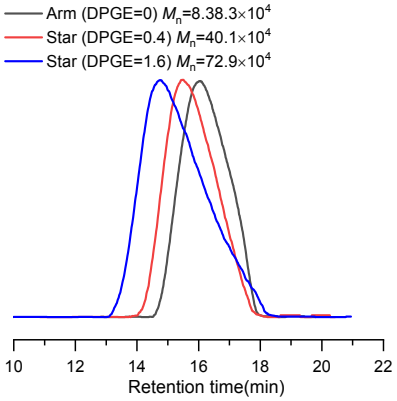


Fig. S24 GPC traces of star polyethers with longer arms.

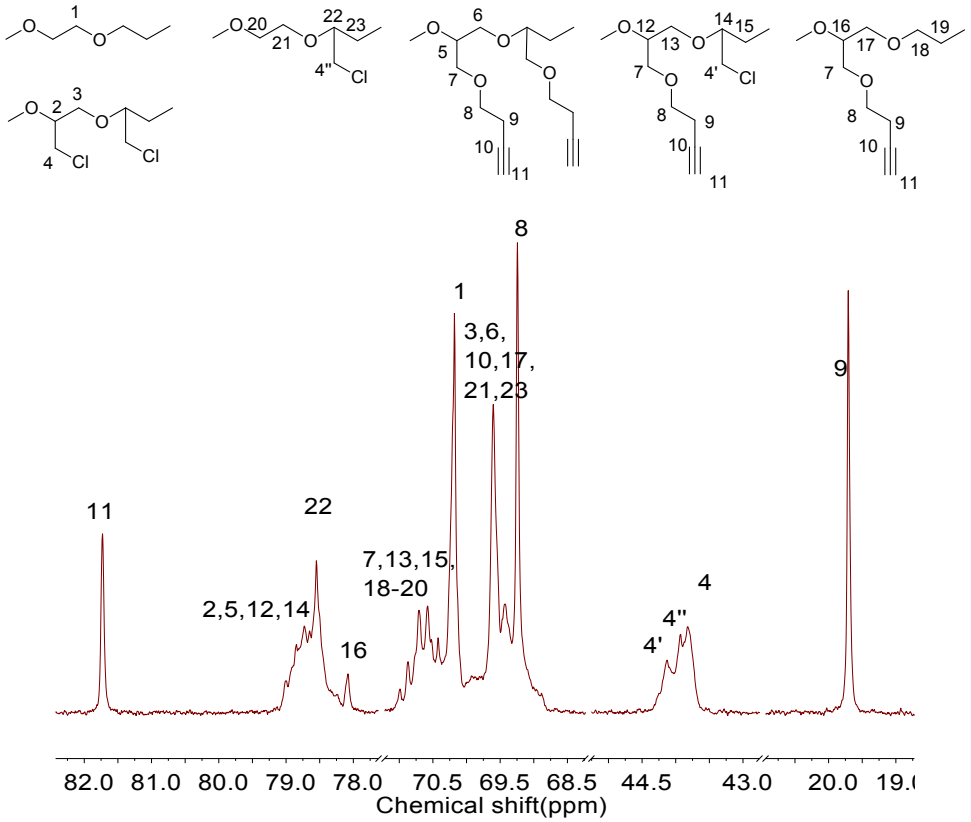


Fig. S25 ^{13}C-NMR spectrum of a star polyether.