Supporting Information for

One pot synthesis and characterization of novel poly(ether ester) mutiblock copolymers containing poly(tetramethylene oxide) and poly(ethylene terephthalate)

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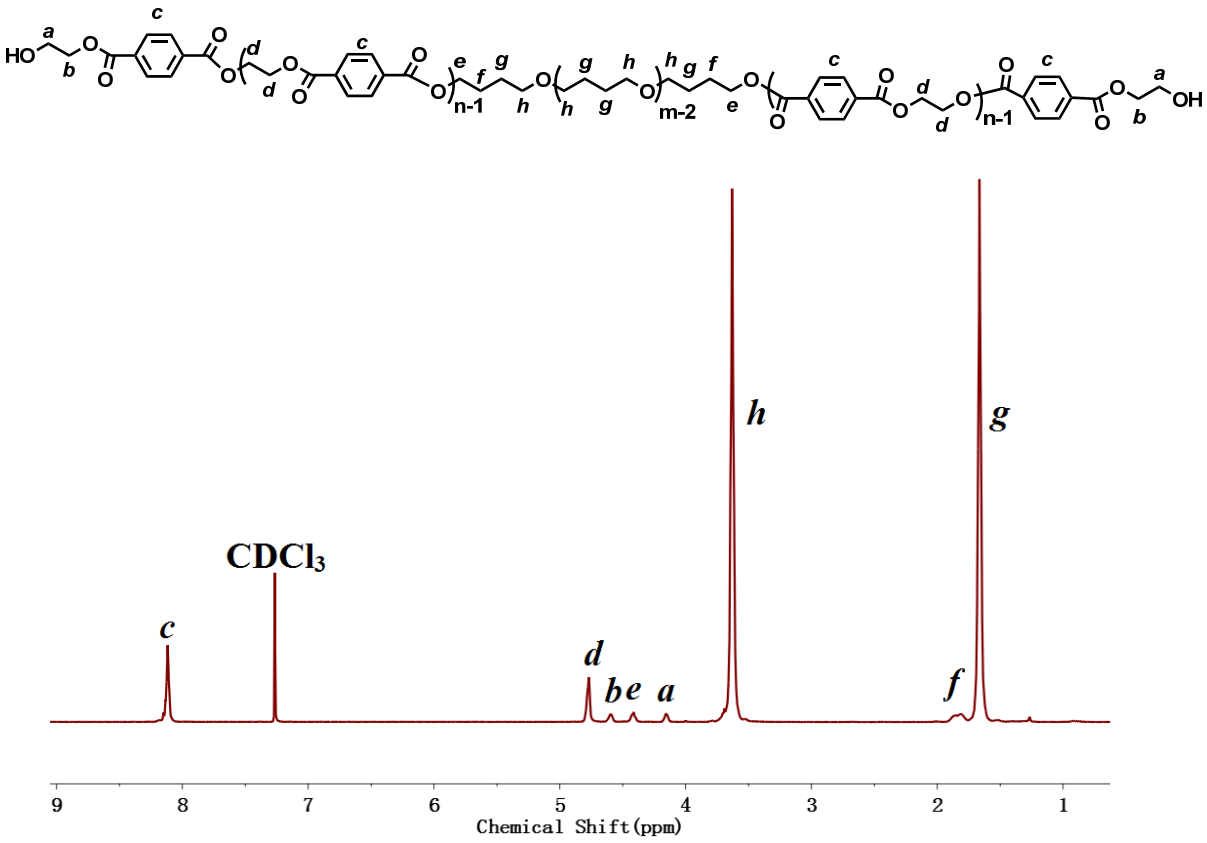

Fig. S1 ^{1}H NMR spectra of PET-*b*-PTMO-*b*-PET triblock copolymer. Solvent: $CF_3COOD/CDCl_3$ (1/10 in volume); concentration: 0.02 g/mL. Polymerization conditions: m_{PTMO}/m_{COETs} = 3/1 with 0.075 wt% Ti(*n*-$C_4H_9O)_4$ hot-pressed at 270 °C under a 10 MPa pressure for 90 minutes.

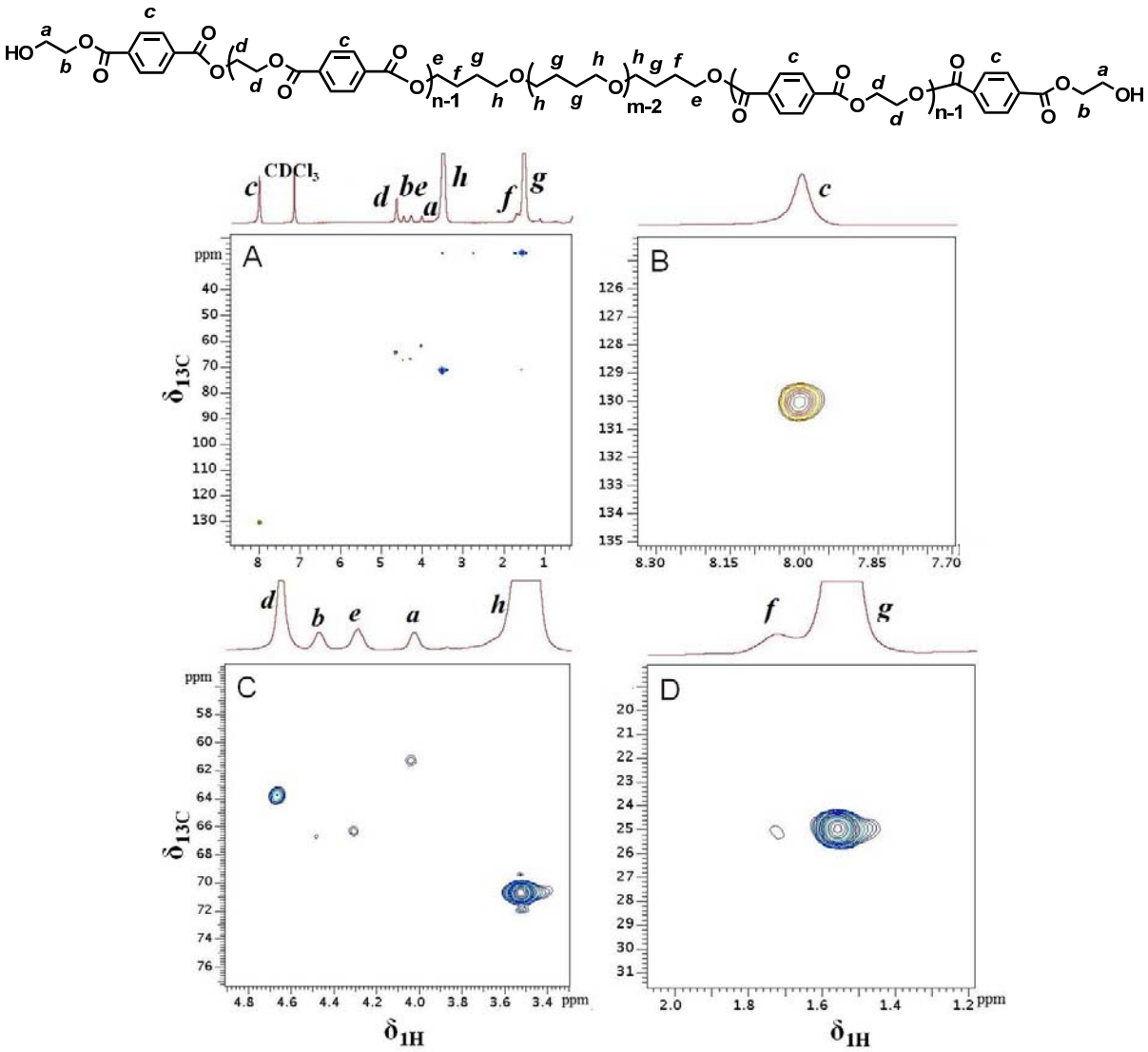

Fig. S2 Two dimensional ^{1}H-^{13}C HSQC spectra of PET-*b*-PTMO-*b*-PET triblock copolymer, with the whole spectra (A), and selected enlarged regions (B, C and D). Solvent: $CF_3COOD/CDCl_3$ (1/10 in volume); concentration: 0.02 g/mL.

Table S1 The integration value of peaks for (PET-*b*-PTMO-*b*-PET)$_x$ multiblock copolymers with 0.075 wt% Ti(*n*-$C_4H_9O)_4$ at 270 °C at different reaction time by ^{1}H NMR.

Sample	Reaction time (min)	*a* 4.16	*b* 4.60	*c* 8.12	*d* 4.78	*e* 4.42	*f*+*g* 1.67-1.86	*h* 3.64
P1-1	15	4.00	4.05	51.0	35.1	9.65	417	408
P1-2	30	4.00	4.34	104	72.2	19.7	854	847
P1-3	45	4.00	4.52	184	132	35.7	1510	1490
P1-4	60	4.00	4.68	270	200	52.9	2250	2210
P1-5	90	4.00	4.79	482	354	94.1	3980	3890

Table S2 The integration value of peaks for (PET-*b*-PTMO-*b*-PET)$_x$ multiblock copolymers at different reaction time by ^{1}H NMR and the corresponding structures calculated. Polymerization condition: 0.15 wt% Ti(*n*-$C_4H_9O)_4$ at 270 °C.

δ (ppm)	Reaction time (min)	*a* 4.16	*b* 4.60	*c* 8.12	*d* 4.78	*e* 4.42	*f*+*g* 1.67-1.86	*h* 3.64	N_{TMO}	N_{ET}	S_{TMO}	S_{ET}	*x*	M_n(kg/mol)
P2-1	15	4.00	4.91	56.7	40.1	11.3	464	456	117	10.0	41.4	3.55	2.83	10.3
P2-2	30	4.00	5.36	119	90.1	23.7	972	962	246	22.5	41.6	3.80	5.93	22.0
P2-3	45	4.00	5.82	191	144	39.2	1550	1540	395	36.0	41.3	3.77	9.55	35.4
P2-4	60	4.00	6.07	296	226	58.5	2370	2350	602	56.5	41.2	3.86	14.6	54.2
P2-5	90	4.00	6.49	537	423	105	4220	4210	1080	106	41.1	4.03	26.3	98.1

$M_{n,}$: number-average molecular weights of polymers by means of NMR.

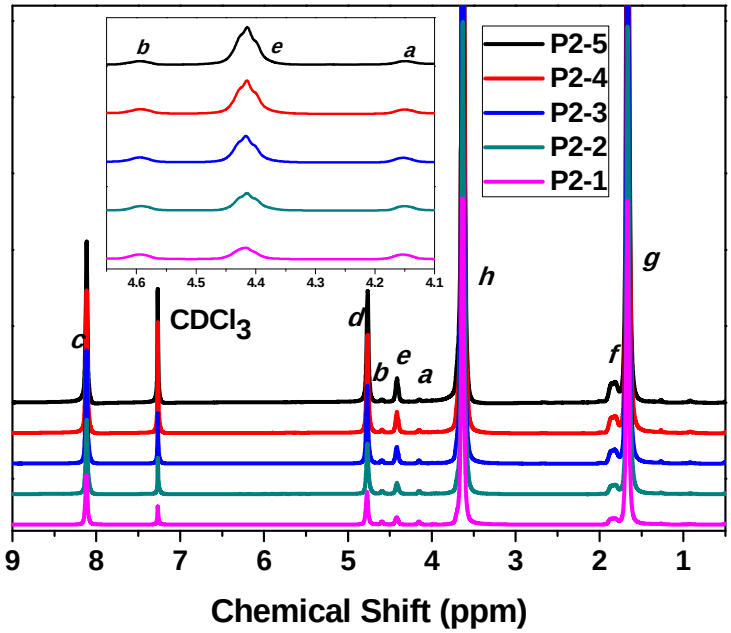

Fig. S3 ^{1}H NMR spectra of (PET-*b*-PTMO-*b*-PET)$_x$ multiblock copolymers synthesized at different reaction time: 15 min (P2-1), 30 min (P2-2), 45 min (P2-3), 60 min (P2-4), 90 min (P2-5). Polymerization condition: 0.15 wt% Ti(*n*-$C_4H_9O)_4$ at 270 °C. Solvent: $CF_3COOD/CDCl_3$ (1/10 in volume); concentration: 0.02 g/mL.

Table S3 The integration value of peaks for (PET-*b*-PTMO-*b*-PET)$_x$ multiblock copolymers at different reaction time by ^{1}H NMR and the corresponding structures calculated. Polymerization condition: 0.075 wt% Ti(*n*-$C_4H_9O)_4$ at 280 °C.

Sample	Reaction time (min)	*a* 4.16	*b* 4.60	*c* 8.12	*d* 4.78	*e* 4.42	*f*+*g* 1.67-1.86	*h* 3.64	N_{TMO}	N_{ET}	S_{TMO}	S_{ET}	*x*	M_n(kg/mol)
P3-1	15	4.00	4.48	53.7	43.2	11.6	436	432	111	10.8	38.2	3.72	2.90	10.1
P3-2	30	4.00	5.28	124	95.6	27.1	1010	1000	257	23.9	37.9	3.53	6.78	23.1
P3-3	45	4.00	5.74	186	151	41.3	1490	1480	380	37.8	36.8	3.66	10.3	34.6
P3-4	60	4.00	6.21	283	220	61.0	2200	2190	563	55.0	36.9	3.61	15.3	51.1
P3-5	90	4.00	6.79	469	373	104	3890	3870	994	93.3	38.2	3.59	26.0	89.5

$M_{n,}$: number-average molecular weights of polymer by means of NMR.

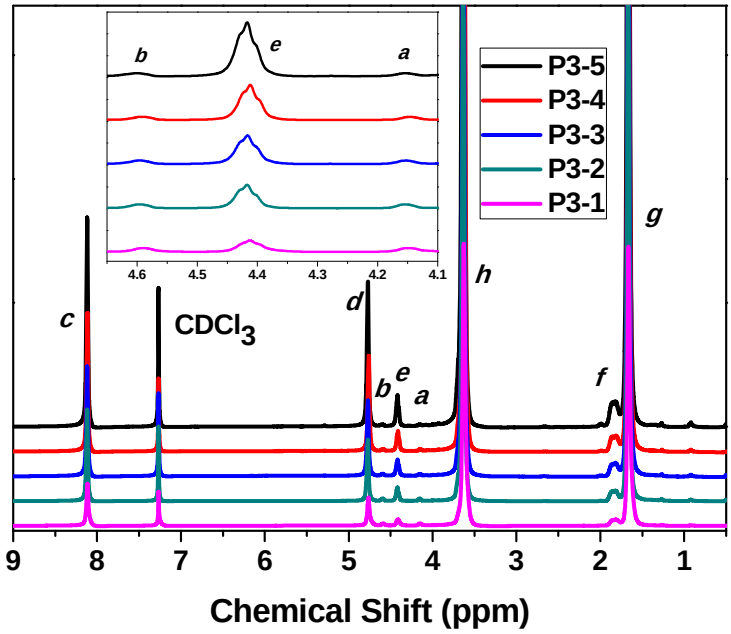

Fig. S4 ^{1}H NMR spectra of (PET-*b*-PTMO-*b*-PET)$_x$ multiblock copolymers synthesized at different reaction time: 15 min (P3-1), 30 min (P3-2), 45 min (P3-3), 60 min (P3-4), 90 min (P3-5). Polymerization condition: 0.075 wt% Ti(*n*-$C_4H_9O)_4$ at 280 °C. Solvent: $CF_3COOD/CDCl_3$ (1/10 in volume); concentration: 0.02 g/mL.

Deduction of equation 6:

$$\text{PET-}b\text{-PTMO-}b\text{-PET} + \text{PET-}b\text{-PTMO-}b\text{-PET} \xrightarrow{k} (\text{PET-}b\text{-PTMO-}b\text{-PET})_2 + \text{EG}$$

$$\text{PET-}b\text{-PTMO-}b\text{-PET} + (\text{PET-}b\text{-PTMO-}b\text{-PET})_2 \xrightarrow{k} (\text{PET-}b\text{-PTMO-}b\text{-PET})_3 + \text{EG}$$

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Assuming each chain end groups have the same reactivity, then we will have the following kinetics equation:

$$-\frac{dc}{dt} = kc^2$$

where c is the concentration of functional end group, t is the reaction time, and k is the reaction constant, which related to the catalyst concentration and temperature. Integration of the above equation will give:

$$\int -\frac{dc}{c^2} = \int k dt$$

$$\frac{1}{c_t} - \frac{1}{c_0} = kt$$

where c_0 and c_t are the corresponding concentration of functional groups at initiate time and time t, respectively. The above equation can be rewritten as:

$$\frac{c_0}{c_t} = kc_0t + 1$$

The degree of polymerization, X_n, can be deduced by its definition:

$$X_n = \frac{c_0}{c_t} = kc_0t + 1 = k't + 1$$