Electronic Supplementary Information for:

The "solid-state" ring-opening cationic polymerization of 1,3,5-trioxane: Frozen polymerization for suppression of oligomer formation and synthesis of ultrahigh molecular weight polymers

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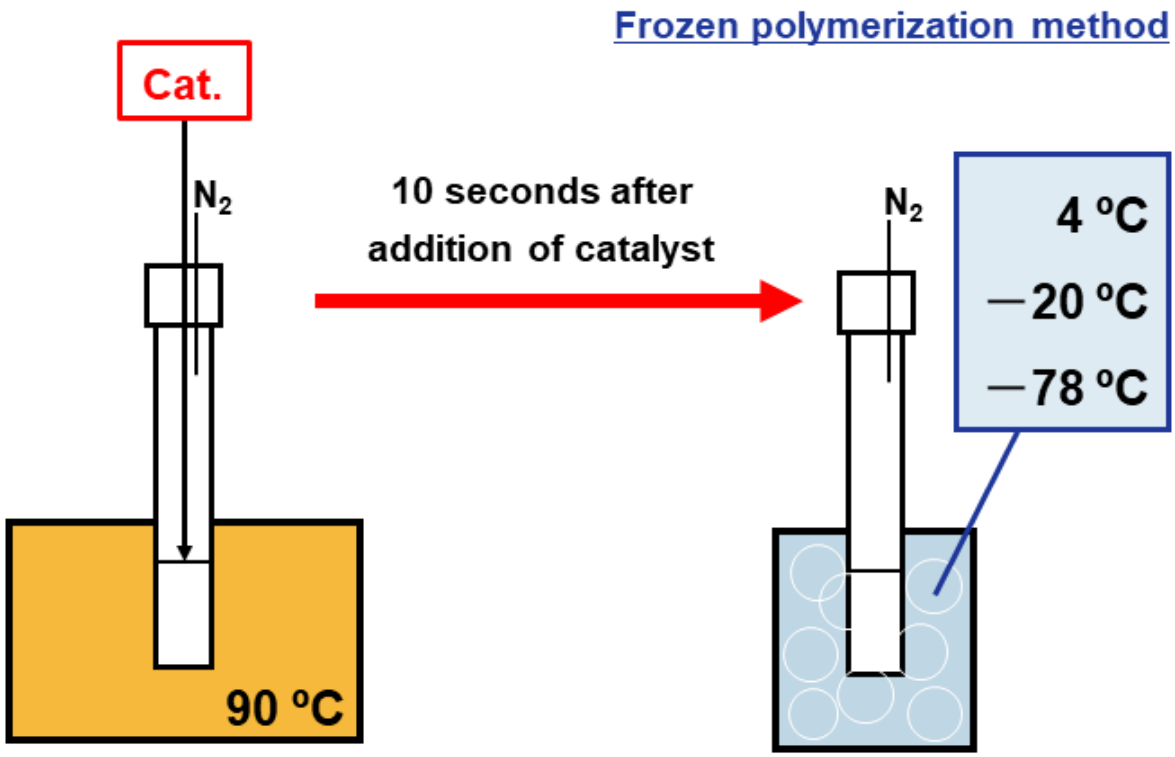

Figure S1. The experimental method of "frozen polymerization".

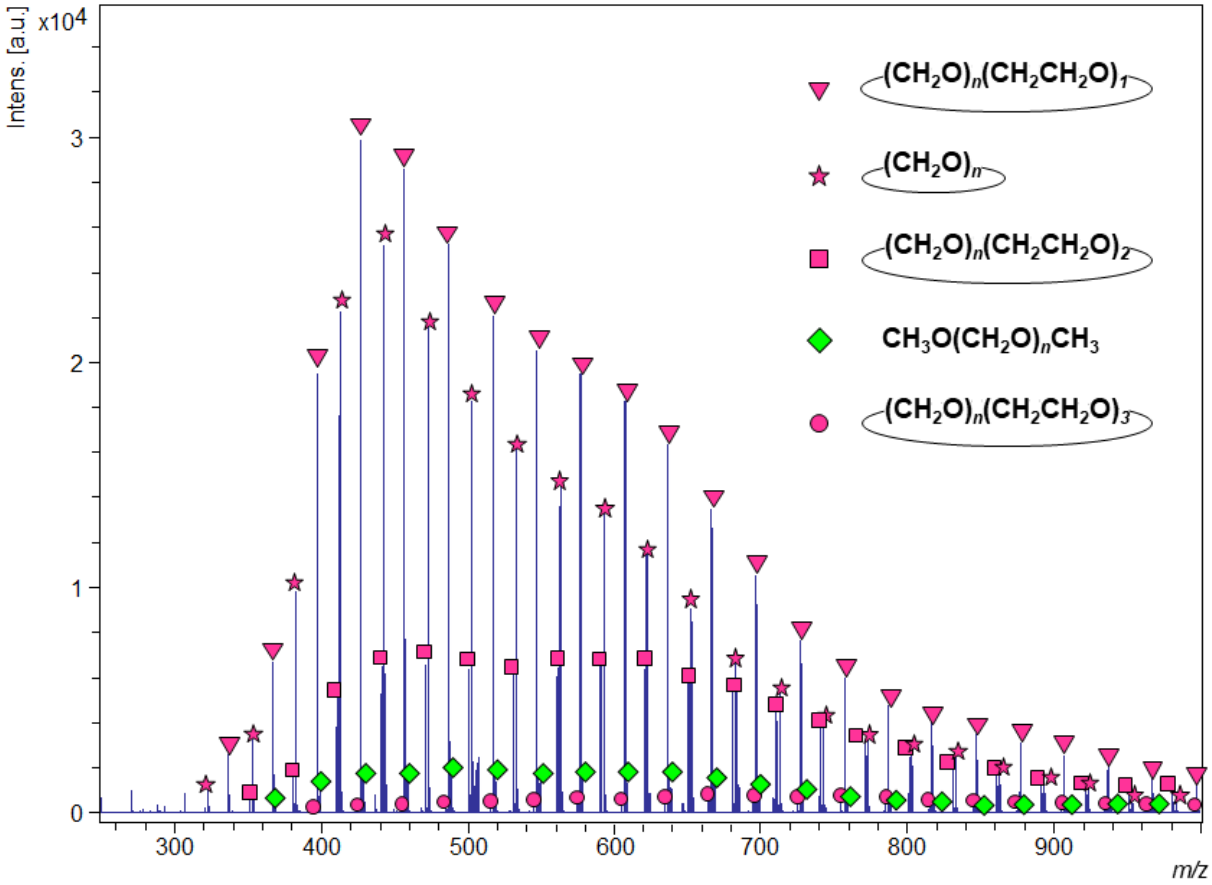

Figure S2. MALDI-TOF-MS spectrum of a POM copolymer sample obtained under conditions similar to those for molten-state homopolymerization of TOX (initial feed ratio: TOX = 96 mol%, 1,3-dioxolane = 4 mol%): $[\text{catalyst}]_0/[\text{monomer}]_0 = 7 \times 10^{-5}$, for 30 s, at 90 ºC.

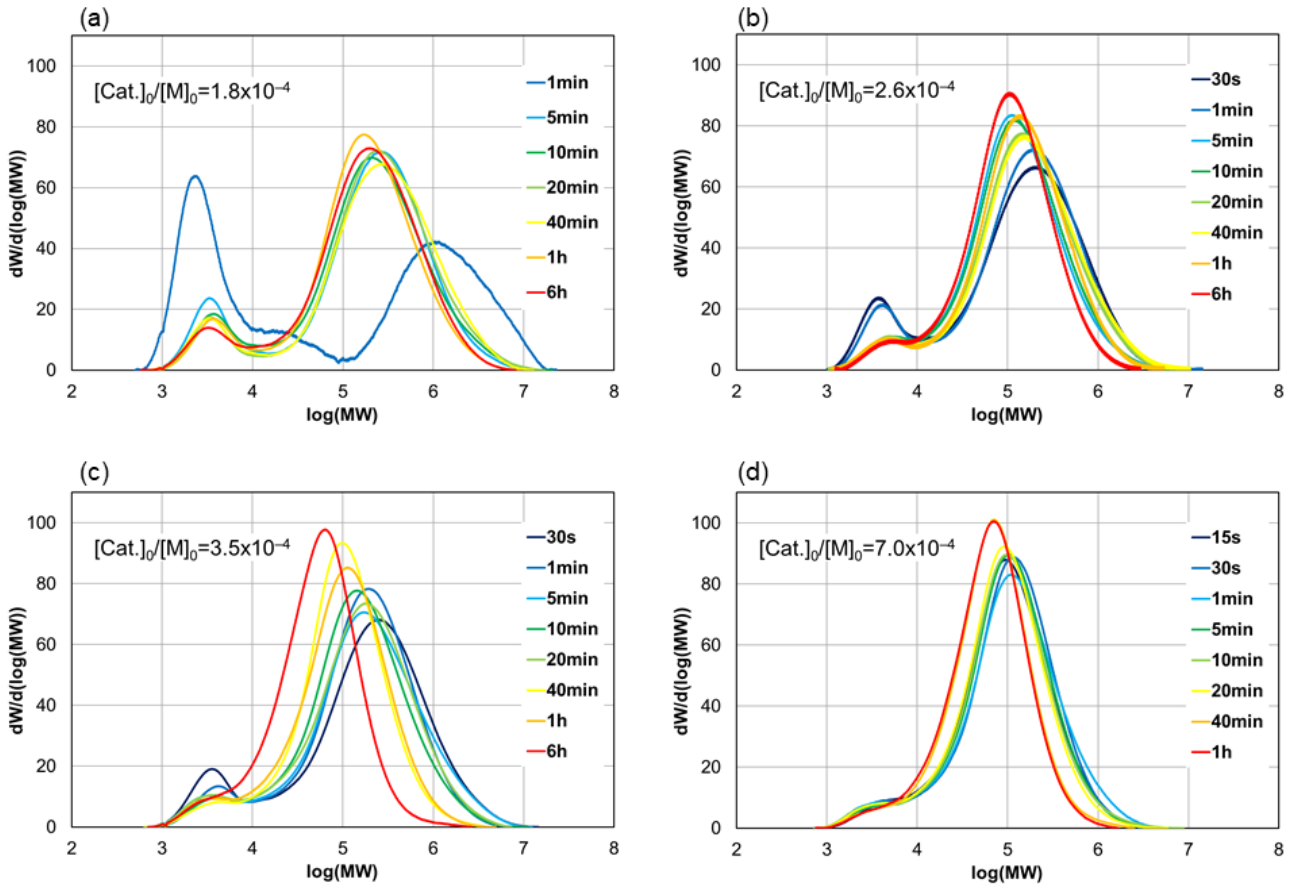

Figure S3. MWD curves of the polymers obtained in the molten-state polymerization of TOX: $[catalyst]_0/[monomer]_0$ = (a) 1.8×10^{-4}, (b) 2.6×10^{-4} (the same data as those shown in Figure 4(c)), (c) 3.5×10^{-4}, or (d) 7.0×10^{-4}, for 15 s—6 h, at 90 ºC.

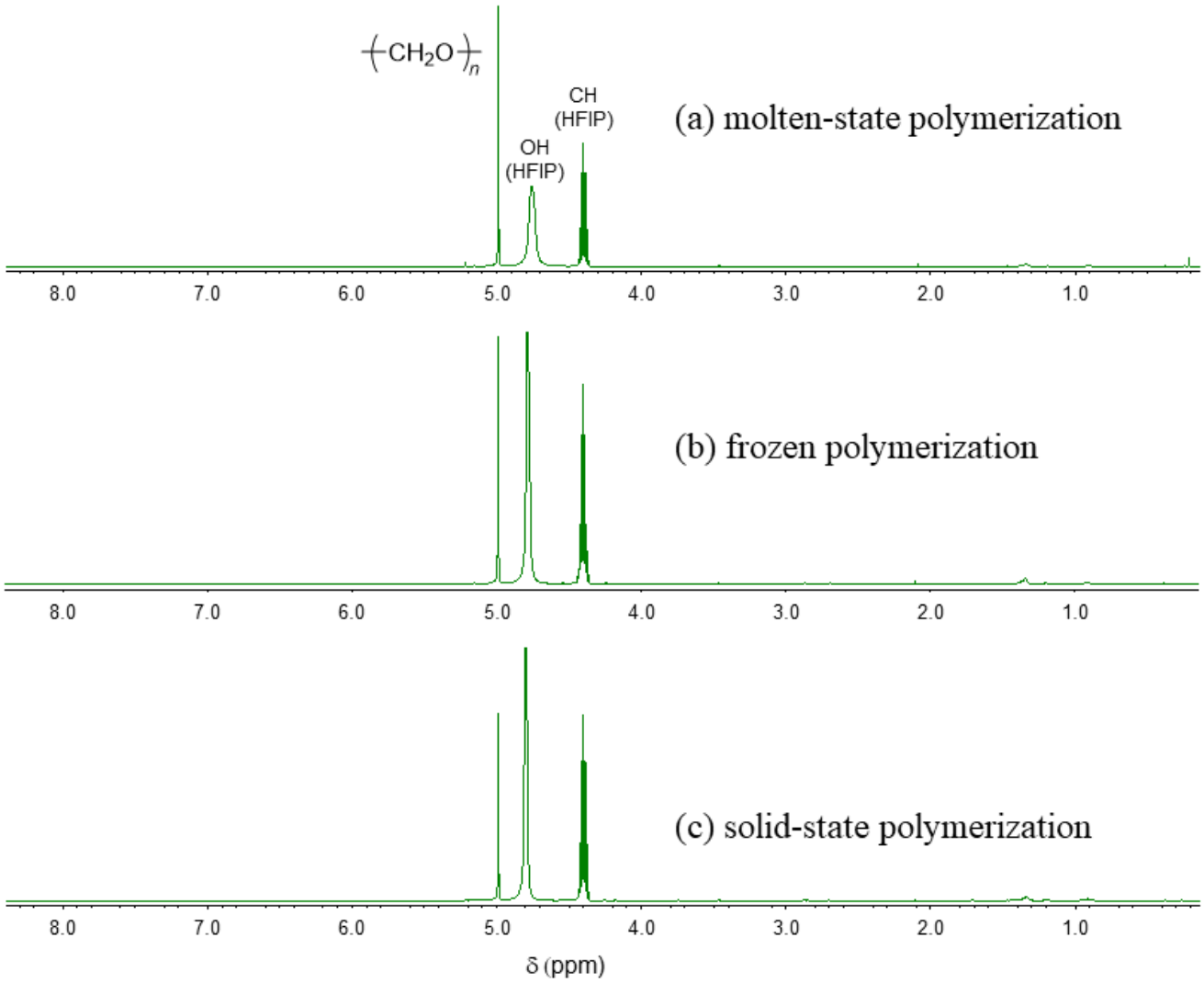

Figure S4. ^{1}H NMR spectra of the polymers obtained in (a) molten-state polymerization (polymerization temperature: 90 °C), (b) frozen polymerization (90 °C → 4 °C), and solid-state polymerization (50 °C): $[\text{catalyst}]_0/[\text{monomer}]_0 = 2.6 \times 10^{-4}$, for 30 min.

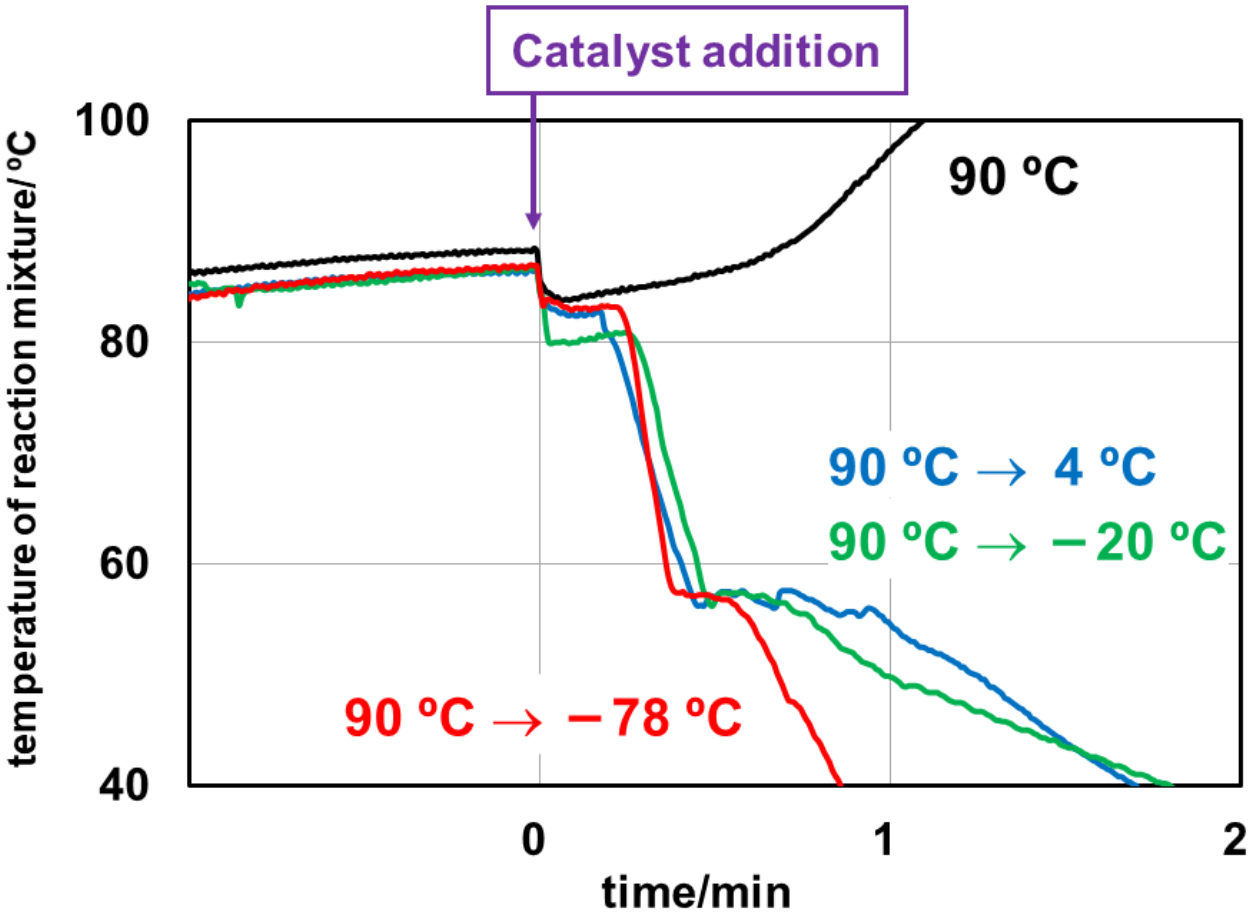

Figure S5. Enlarged view of temperature transition in polymerization systems: $[catalyst]_0/[monomer]_0 = 2.6 \times 10^{-4}$, for 30 min, Initial temperature (oil bath): 90 ºC. The same data as those shown in Figure 3.

Table S1. Reproducibility of molten-state polymerization and frozen polymerization[a]

Entry	Polymerization temperature	Yield	Oligomer ratio	M_w ($\times 10^6$)	M_p ($\times 10^6$)	M_w/M_n	T_m
1	90 °C (molten-state polymerization)	89 %	6.5 %	0.16	0.10	5.2	183 ºC
2		86 %	6.5 %	0.20	0.11	6.1	181 ºC
3		89 %	6.5 %	0.22	0.13	6.8	182 ºC
4		88 %	7.5 %	0.24	0.14	8.0	181 ºC
5		84 %	6.8 %	0.22	0.14	7.0	182 ºC
6	90 °C → 4 °C (frozen polymerization)	58 %	5.8 %	0.88	0.41	25	188 ºC
7		85 %	5.4 %	1.2	0.54	30	188 ºC
8		85 %	4.8 %	1.1	0.49	26	190 ºC
9		78 %	5.2 %	1.0	0.50	28	189 ºC
10		86 %	5.3 %	1.1	0.59	29	188 ºC

[a] $[\text{catalyst}]_0/[\text{monomer}]_0 = 2.6 \times 10^{-4}$, for 30 min.

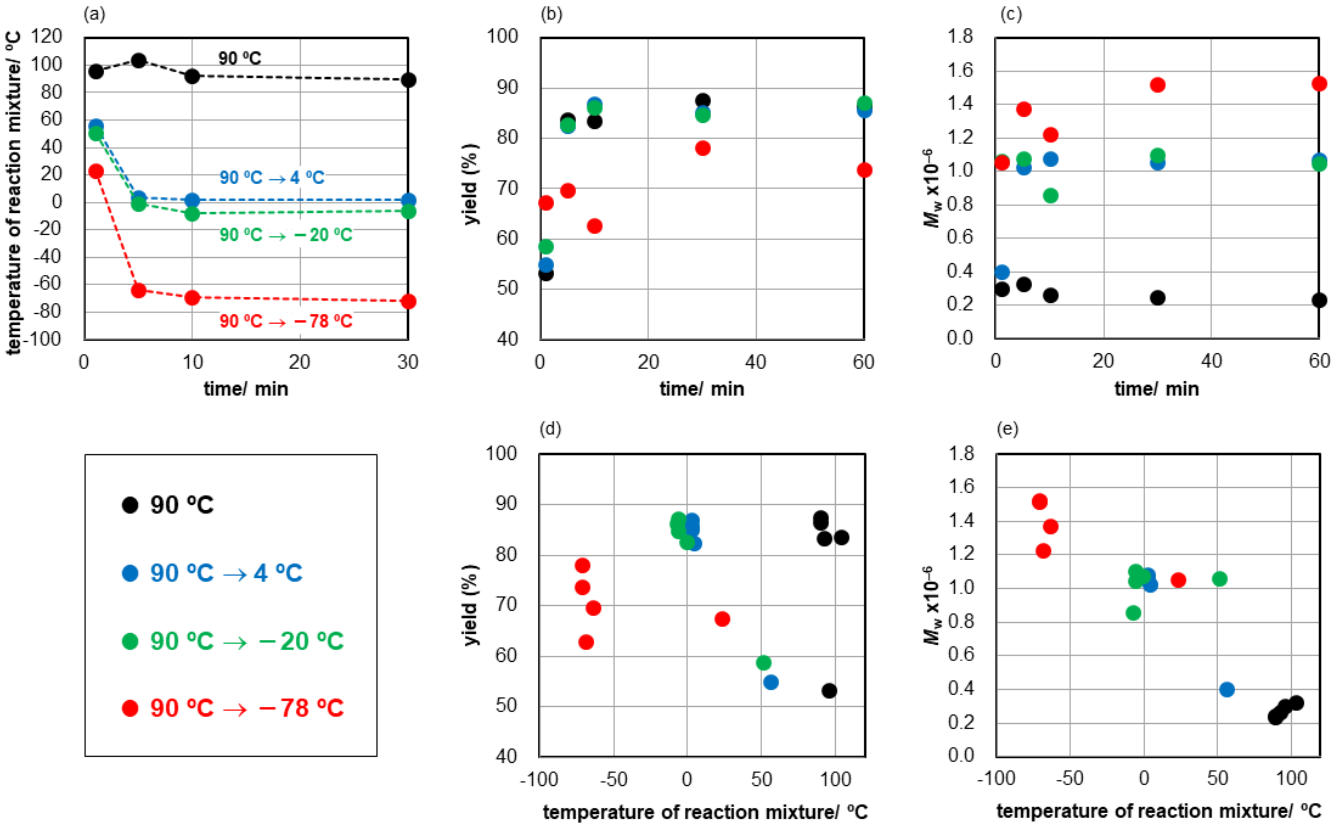

Figure S6. The relationships between (a) reaction time and temperature of reaction mixture; (b) reaction time and yield; (c) reaction time and M_w; (d) temperature of reaction mixture and yield; and (e) temperature of reaction mixture and M_w in the molten-state polymerization and frozen polymerization of TOX: $[\text{catalyst}]_0/[\text{monomer}]_0 = 2.6 \times 10^{-4}$, for 1—60 min.

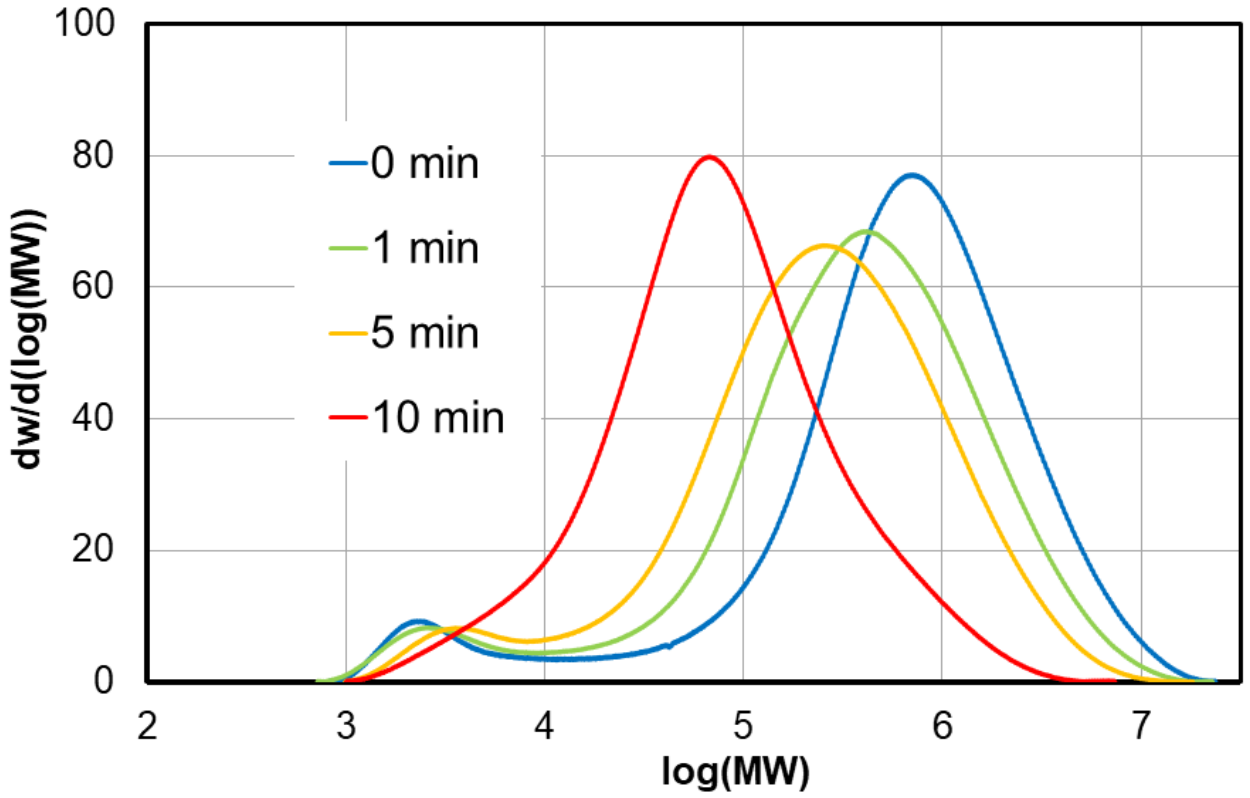

Figure S7. MWD curves of the polymers obtained by heating the reaction mixture for 1—10 min at 140 ºC without quenching frozen polymerization of TOX: $[catalyst]_0/[monomer]_0 = 2.6 \times 10^{-4}$, frozen polymerization was conducted at 4 ºC.

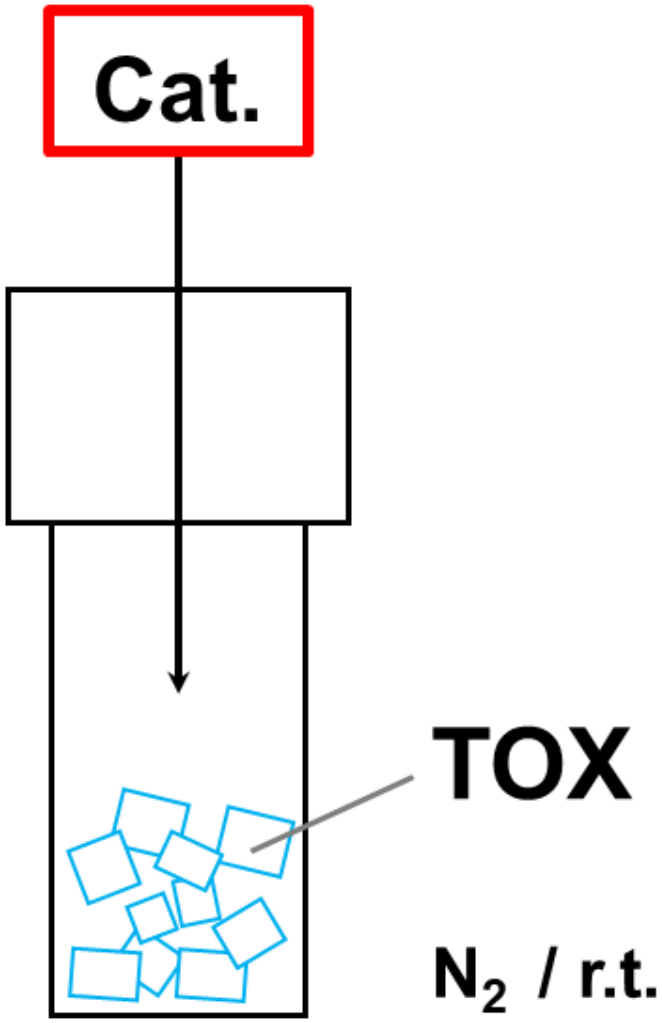

Figure S8. The experimental method of solid-state polymerization.

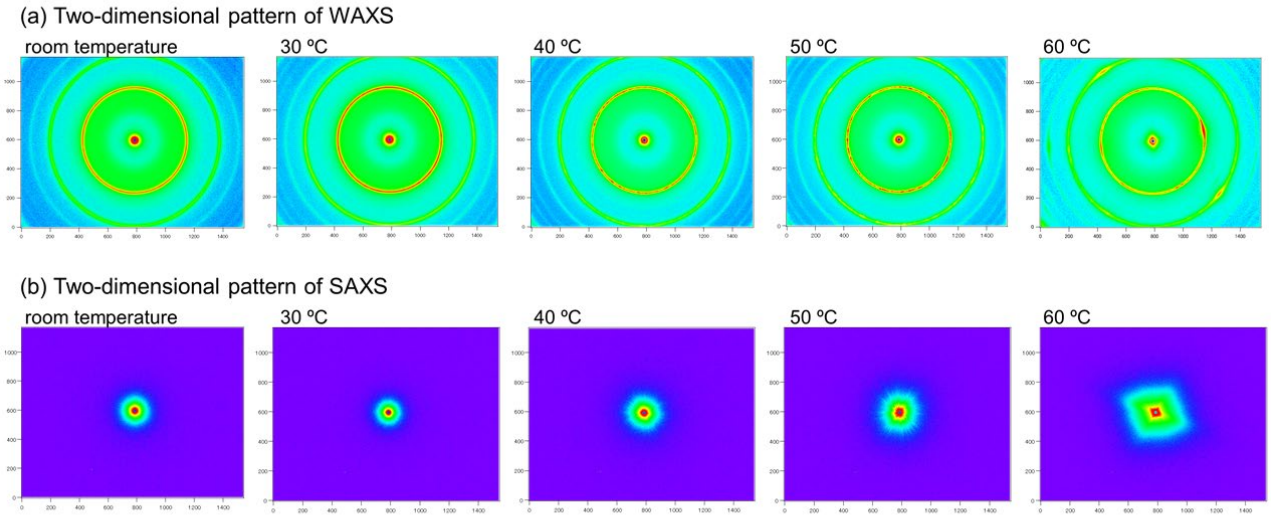

Figure S9. Two-dimensional pattern of (a) WAXS and (b) SAXS of the polymers obtained in the solid-state polymerization: $[\text{catalyst}]_0/[\text{monomer}]_0 = 2.6 \times 10^{-4}$, for 30 min, at room temperature—60 ºC.

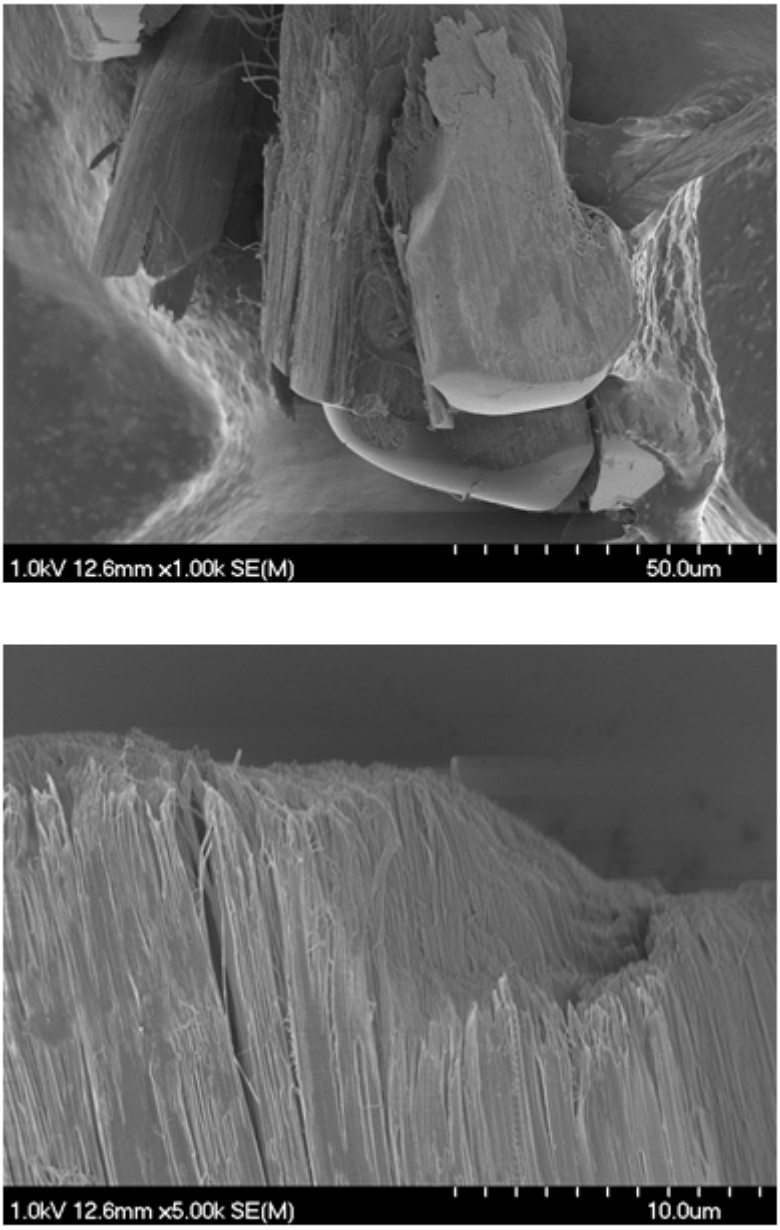

Figure S10. SEM images of the polymers obtained in the solid-state polymerization (50 ºC): $[catalyst]_0/[monomer]_0 = 2.6 \times 10^{-4}$, for 30 min.