

Supporting Information

Precise Control of Lower Critical Solution Temperature of Thermo-sensitive Poly(2-isopropyl-2-oxazoline) (PiPrOx) via Gradient Copolymerization with 2-Ethyl-2-oxazoline as a Hydrophilic Comonomer

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78 hrs

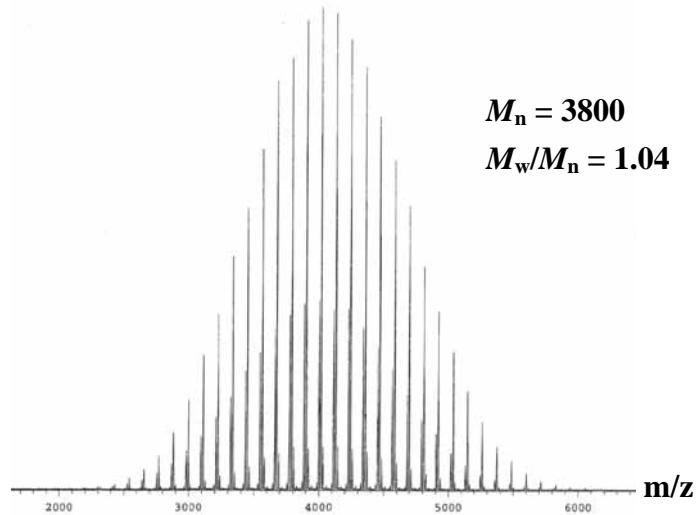


Figure S1-(a). MALDI-TOF mass spectrum of Me-PiPrOx-OH after 78 hrs.

94.5 hrs

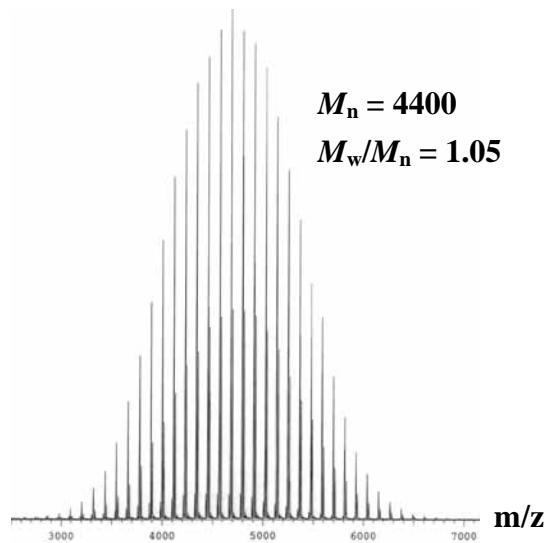


Figure S1-(b). MALDI-TOF mass spectrum of Me-PiPrOx-OH after 94.5 hrs.

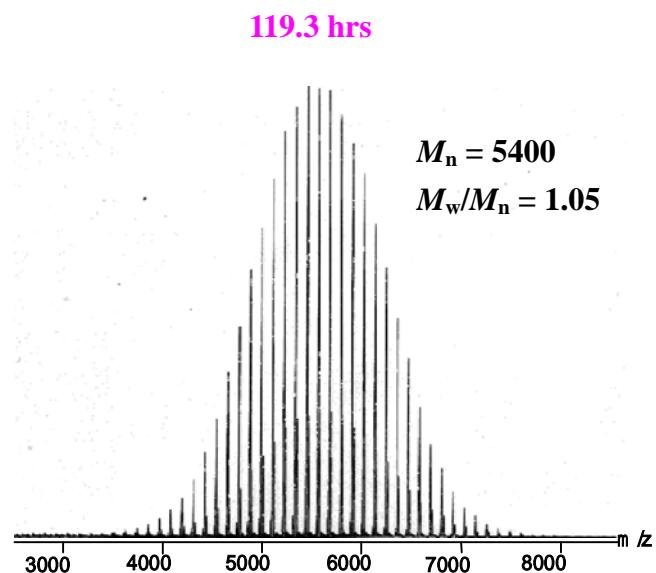


Figure S1-(c). MALDI-TOF mass spectrum of Me-PiPrOx-OH after 119.3 hrs.

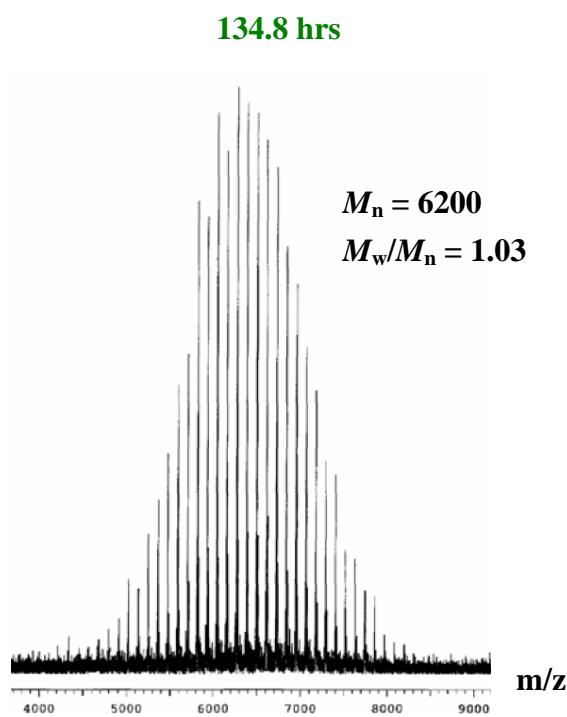


Figure S1-(d). MALDI-TOF mass spectrum of Me-PiPrOx-OH after 134.8 hrs.

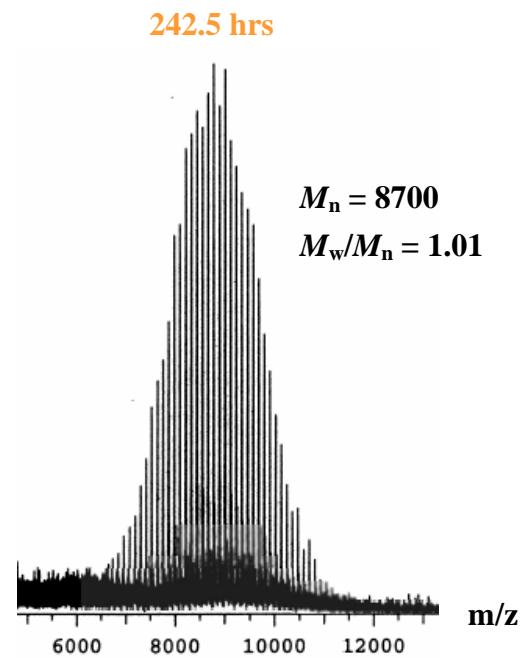


Figure S1-(e). MALDI-TOF mass spectrum of Me-PiPrOx-OH after 242.5 hrs.

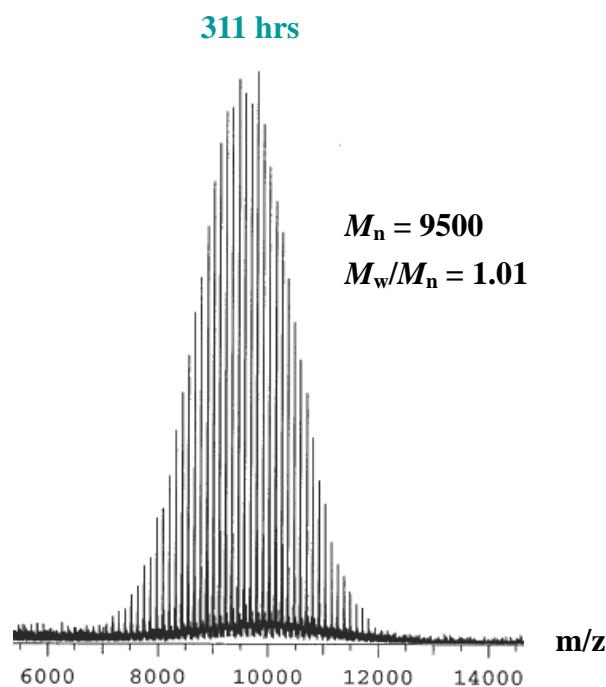


Figure S1-(f). MALDI-TOF mass spectrum of Me-PiPrOx-OH after 311 hrs.

476.5 hrs

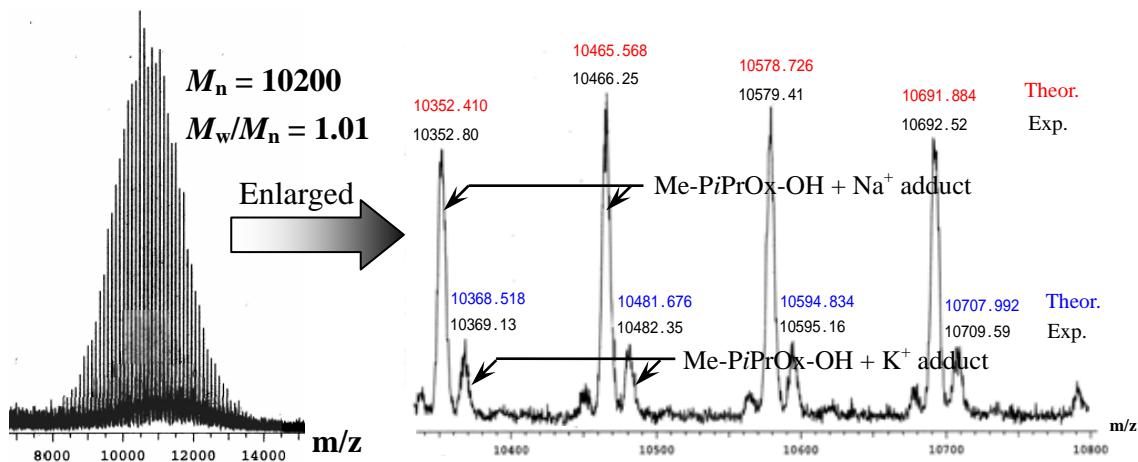


Figure S1-(g). MALDI-TOF mass spectrum of the final product of Me-PiPrOx-OH (left) and its expanded spectrum in the region of 10340 – 10800 (right).

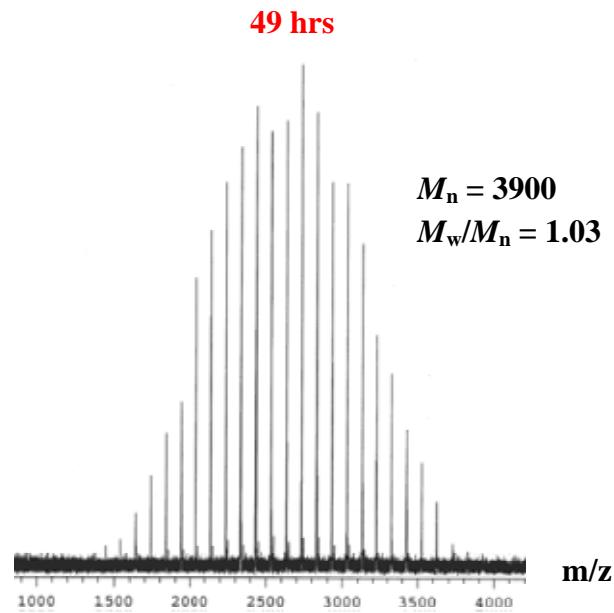


Figure S2-(a). MALDI-TOF mass spectrum of Me-PEtOx-OH after 49 hrs.

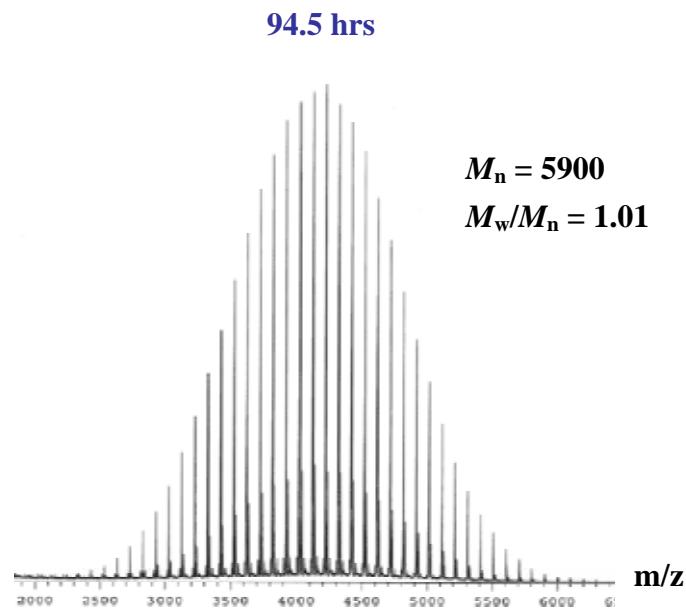


Figure S2-(b). MALDI-TOF mass spectrum of Me-PEtOx-OH after 94.5 hrs.

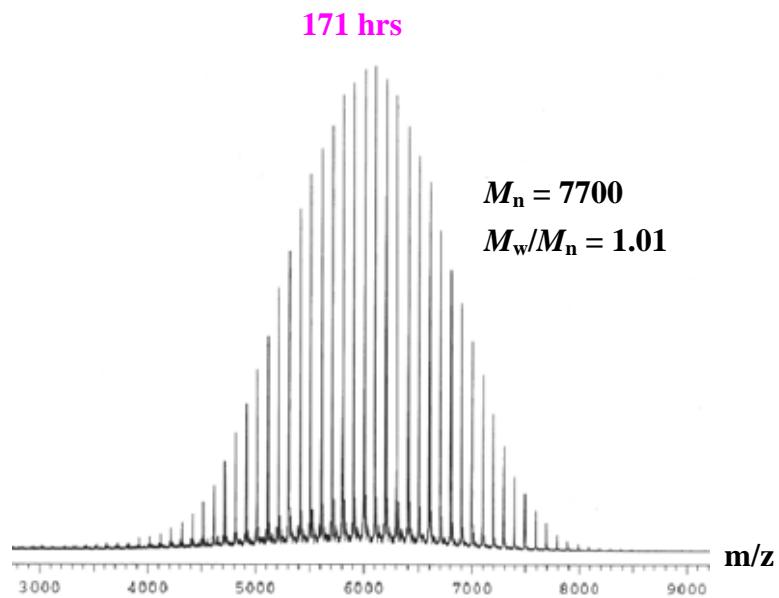


Figure S2-(c). MALDI-TOF mass spectrum of Me-PEtOx-OH after 171 hrs.

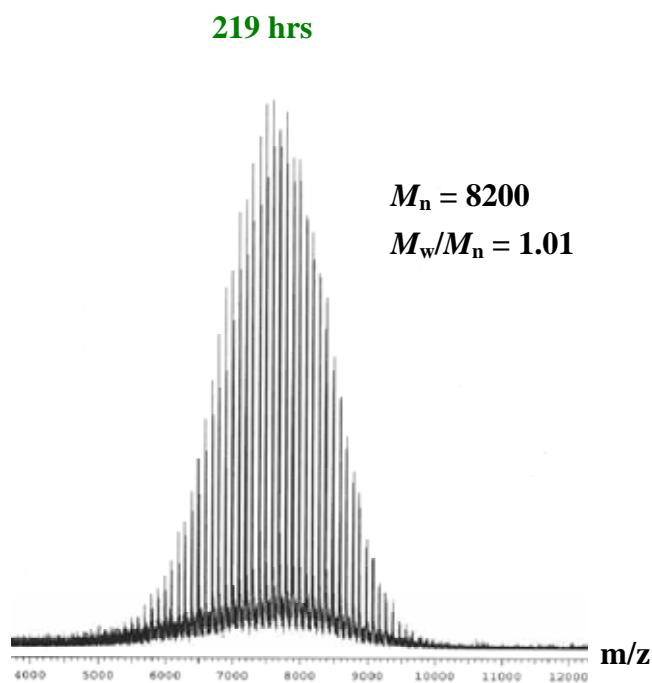


Figure S2-(d). MALDI-TOF mass spectrum of Me-PEtOx-OH after 219 hrs.

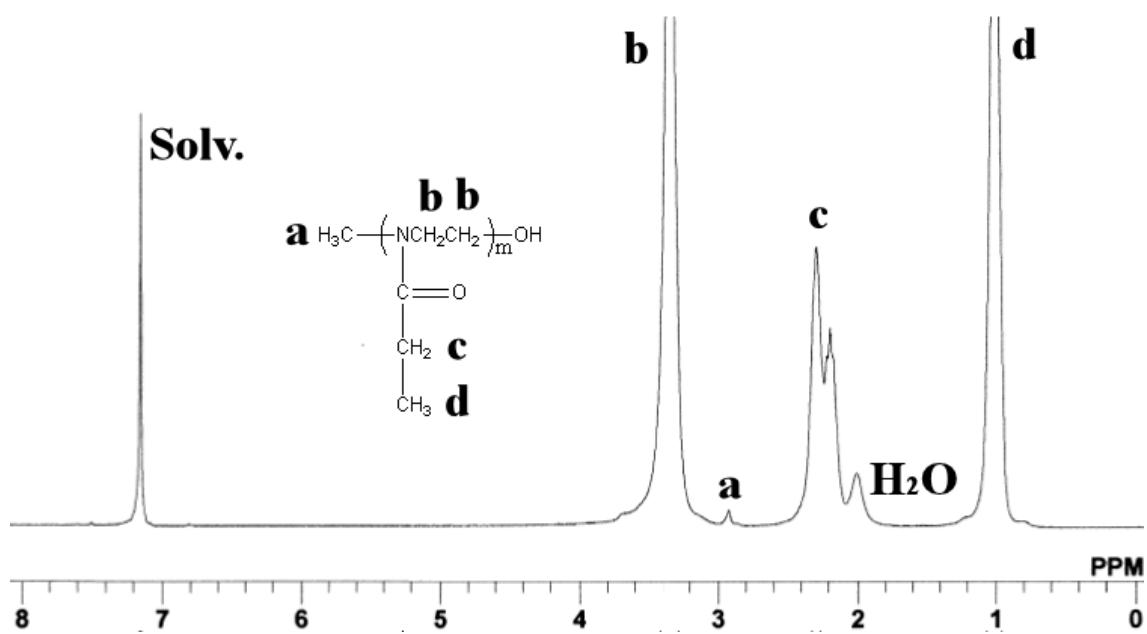


Figure S3. ^1H -NMR spectrum of Me-PEtOx-OH in CDCl_3 at 25°C .

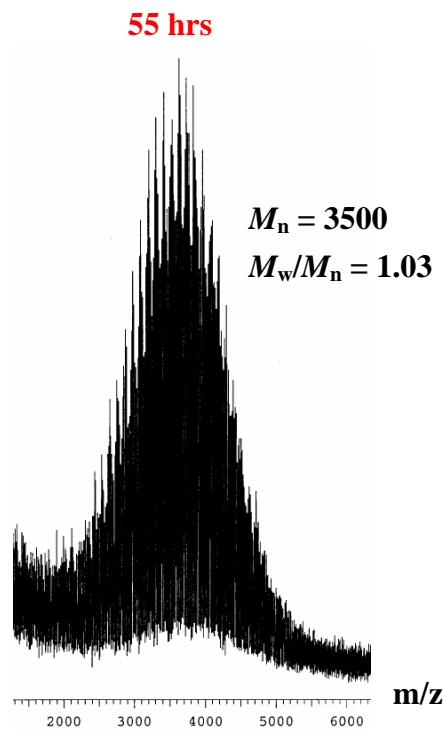


Figure S4-(a). MALDI-TOF mass spectrum of P(EtOx_{25%} iPrOx_{75%}) after 55 hrs.

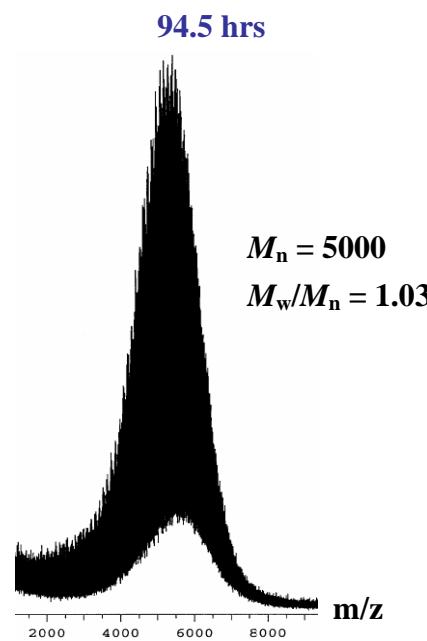


Figure S4-(b). MALDI-TOF mass spectrum of P(EtOx_{25%} iPrOx_{75%}) after 94.5 hrs.

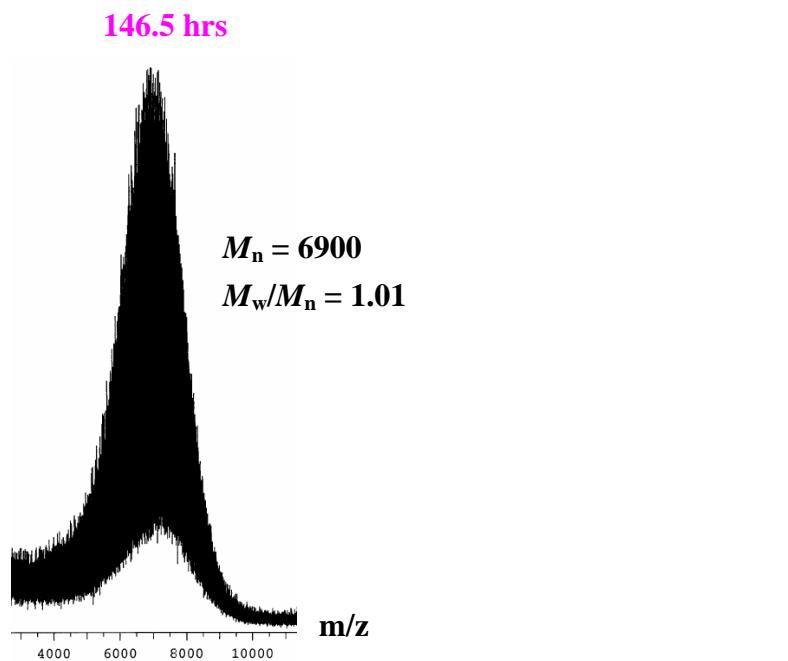


Figure S4-(c). MALDI-TOF mass spectrum of P(EtOx_{25%} iPrOx_{75%}) after 146.5 hrs.

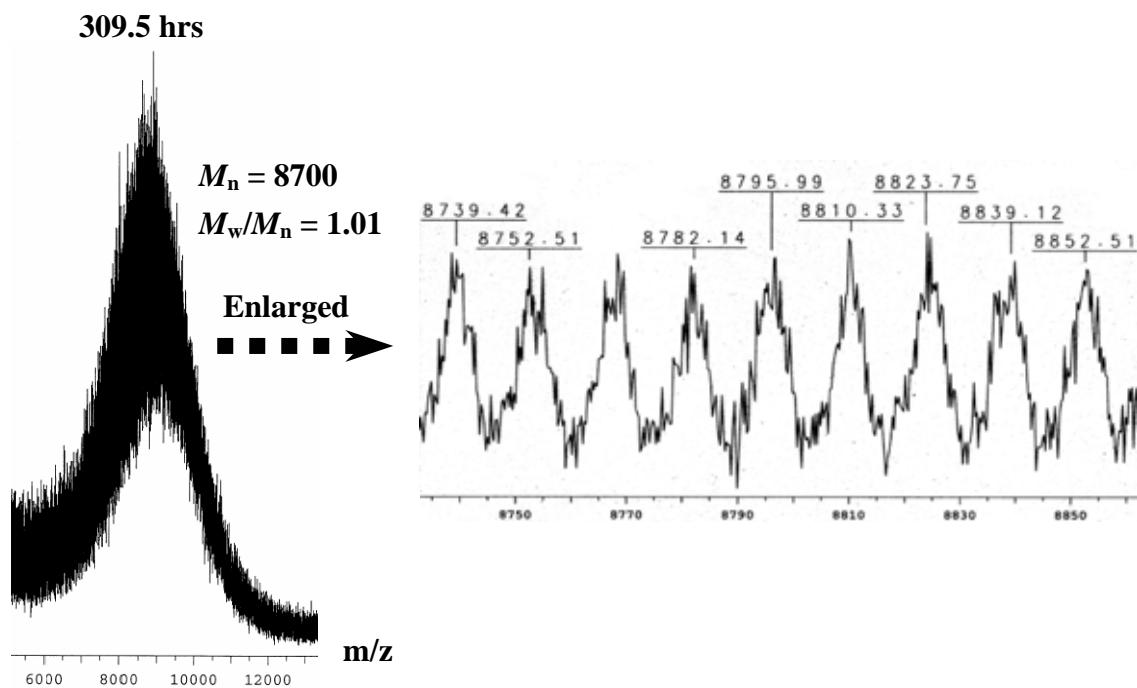


Figure S4-(d). MALDI-TOF mass spectra of P(EtOx_{25%} iPrOx_{75%}) after 309.5 hrs.

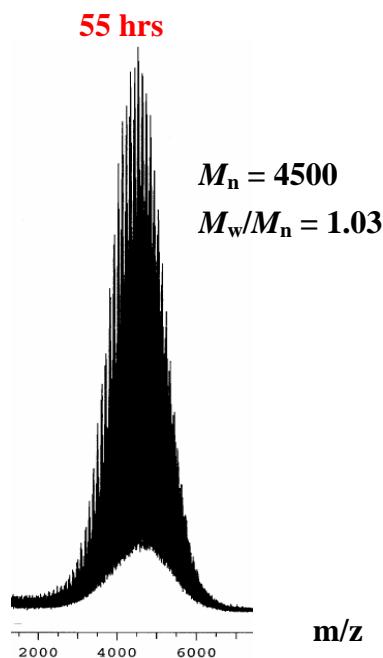


Figure S5-(a). MALDI-TOF mass spectrum of P(EtOx_{75%}*i*PrOx_{25%}) after 55 hrs.

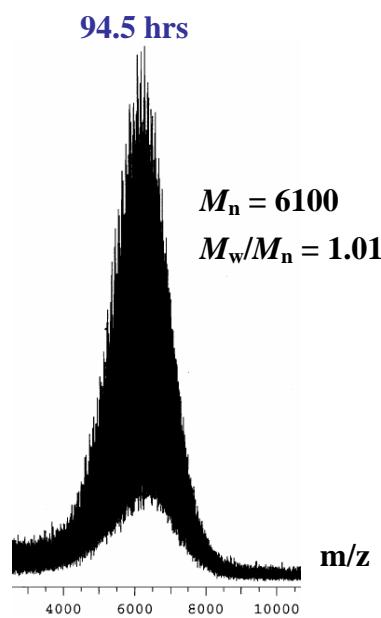


Figure S5-(b). MALDI-TOF mass spectrum of P(EtOx_{75%}*i*PrOx_{25%}) after 94.5 hrs.

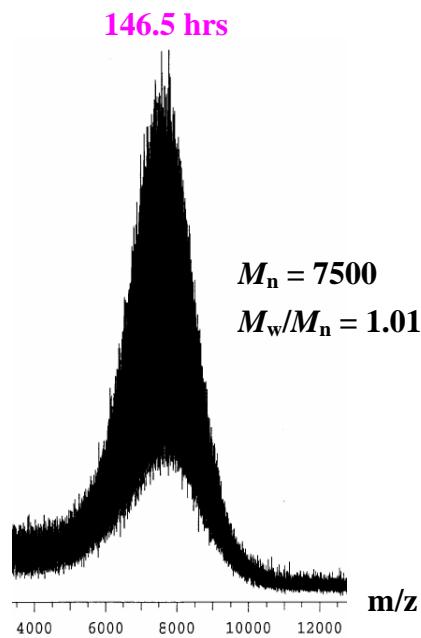


Figure S5-(c). MALDI-TOF mass spectrum of P(EtOx_{75%} iPrOx_{25%}) after 146.5 hrs.

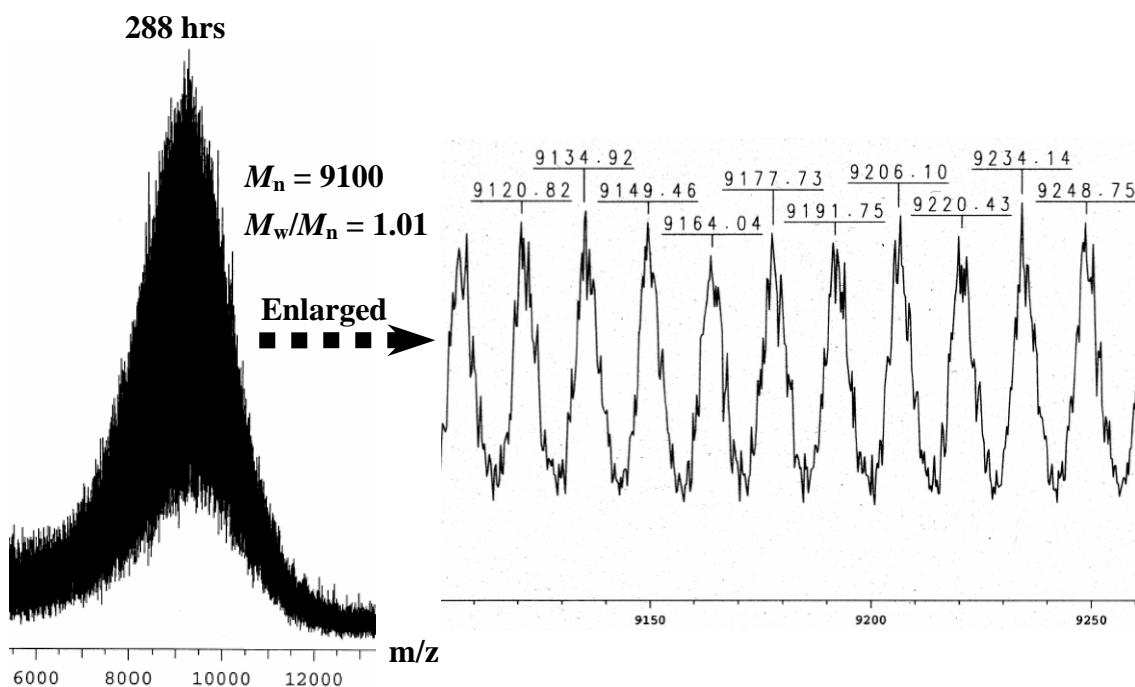


Figure S5-(d). MALDI-TOF mass spectra of P(EtOx_{75%} iPrOx_{25%}) after 288 hrs.

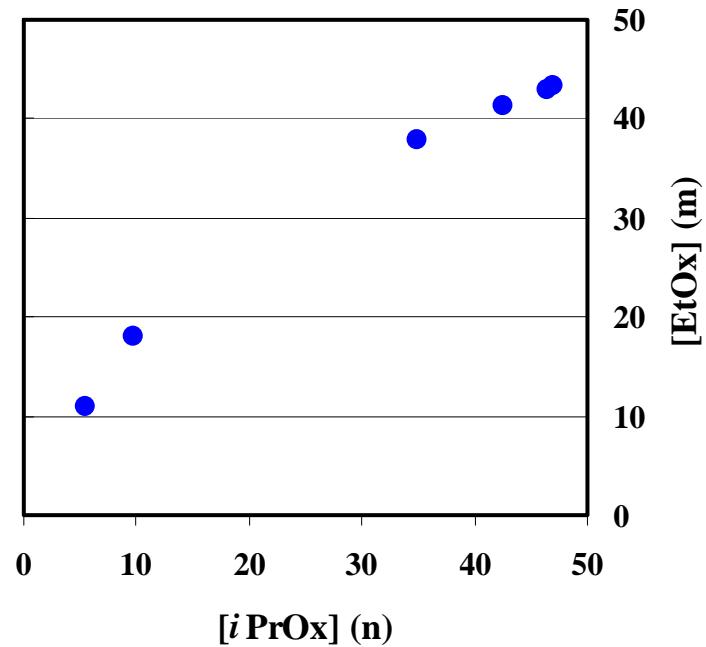


Figure S6. Gradient copolymer fingerprint obtained from ^1H -NMR analysis: trace of six P(EtO_x_{50%}*i*PrO_x_{50%}) samplings after 24, 44, 168, 265, 359, and 407 hrs.

Table S1. Relationship between feed ratios of two monomers and copolymer compositions

run	Monomer mixture			Copolymer composition (Conversion: ca. 20% ~ 40%)		
	[M _{EtOx}]	[M _{iPrOx}]	[M _{EtOx}]/[M _{iPrOx}]	[m _{EtOx}]	[m _{iPrOx}]	[m _{EtOx}]/[m _{iPrOx}]
1	0.25	0.75	0.333	0.302	0.698	0.433
2	0.50	0.50	1.000	0.647	0.353	1.833
3	0.75	0.25	3.000	0.797	0.203	3.926

Table S2. Comparison of the reactivity ratios determined via different calculation methods for the copolymerization of EtOx and *i*PrOx

Calculation method	r_{EtOx}	$r_{i\text{PrOx}}$
(a) The slope-intersection method	1.80	0.70
(b) The Fineman-Ross (FR) method	1.70	0.81
(c) The Yezrielev-Brokhina-Roskin (YBR) method	1.35	0.64
(d) The Kelen-Tüdös (KT) method	1.35	0.61
(e) The Tidwell-Mortimer (TM) method	1.78	0.79

(a) Mayo, F. R.; Walling, C. *Chem. Rev.* **1950**, *46*, 191. (b) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259. (c) Yezrielev, A. I.; Brokhina, E. L.; Roskin, E. S. *Vysokomol. Soedin.* **1969**, *A11*, 1670. (d) Kelen, T.; Tüdös, F. *J. Macromol. Sci. Chem.* **1975**, *A9*, 1. (e) Tidwell, P. W.; Mortimer G. A. *J. Macromol. Sci. Rev. Macromol. Chem.* **1970**, *C4*, 281. (Adopted in this system for the further composition analysis of gradient copolymers)