Electronic Supplementary Information for:

Dual Control of Stereoregularity and Molecular Weight in Cationic Polymerization of Vinyl Ether by Tunable TADDOLs/$TiCl_4$ Initiating Systems

Hironobu Watanabe, Yuji Mishima, Arihiro Kanazawa and Sadahito Aoshima*

Department of Macromolecular Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560-0043, Japan

Contents:

Experimental Section

Procedure for TADDOL Synthesis

The typical procedure for TADDOL synthesis is described as follows:

Magnesium turnings (1.03 g, 42.4 mmol; Nacalai Tesque, ≥99.5%) were added to a two-neck round-bottom flask equipped with a magnetic stir bar and a reflux condenser. The apparatus was dried using a heat gun under a dry nitrogen atmosphere, and a crystal of iodine and THF (40 mL) were added. 4-Bromotoluene (5.19 mL, 42.2 mmol; TCI, >99.0%) was slowly added into the flask at room temperature. After the reaction started, the reaction mixture was heated under reflux for 1.5 h and then cooled at 0 °C. A solution of dimethyl (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (1.67 mL, 9.17 mmol; BLD Pharmatech, 98%) in THF (5.0 mL) was slowly added. The reaction mixture was heated under reflux for 5 h and then cooled at 0 °C. Then, the reaction was quenched with saturated aqueous NH_4Cl (25 mL). After the organic and aqueous layers were separated, the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The product was recrystallized with methanol to give (4*R*,5*R*)-(–)-2,2-Dimethyl-α,α,α',α'-tetra(4-methylphenyl)-1,3-dioxolane-4,5-dimethanol (Me-TADDOL) (3.04 g, 63%). The product was dissolved in hot hexane, and trace amount of residual methanol was completely removed under reduced pressure.

(4R,5R)-(–)-2,2-Dimethyl-α,α,α',α'-tetra(4-methylphenyl)-1,3-dioxolane-4,5-dimethanol (Me-TADDOL)

^{1}H NMR ($CDCl_3$; 500 MHz): δ 7.39 (4H, d), 7.21 (4H, d), 7.11 (4H, d), 7.04 (4H, d), 4.57 (2H, s), 3.73 (2H, s), 2.35 (6H, s), 2.28 (6H, s), 1.06 (6H, s). (3.0 g, yield = 63%)

(4R,5R)-(–)-2,2-Dimethyl-α,α,α',α'-tetra(4-t-butylphenyl)-1,3-dioxolane-4,5-dimethanol (tBu-TADDOL)

^{1}H NMR ($CDCl_3$; 500 MHz): δ 7.44 (4H, d), 7.31 (4H, d), 7.29 (8H, s), 4.57 (2H, s), 3.88 (2H, s), 1.33 (18H, s), 1.27 (18H, s), 1.00 (6H, s). (2.1 g, yield = 66%)

(4R,5R)-(–)-2,2-Dimethyl-α,α,α',α'-tetra(4-methoxyphenyl)-1,3-dioxolane-4,5-dimethanol (MeO-TADDOL)

^{1}H NMR ($CDCl_3$; 400 MHz): δ 7.44 (4H, d), 7.24 (4H, d), 6.86 (4H, d), 6.77 (4H, d), 4.49 (2H, s), 3.92 (2H, s), 3.83 (6H, s), 3.76 (6H, s), 1.07 (6H, s). (3.8 g, yield = 71%)

(4R,5R)-(–)-2,2-Dimethyl-α,α,α',α'-tetra(4-trifluoromethylphenyl)-1,3-dioxolane-4,5-dimethanol (CF_3-TADDOL)

^{1}H NMR ($CDCl_3$; 400 MHz): δ 7.63 (8H, m), 7.52 (4H, d), 7.42 (4H, d), 4.56 (2H, s), 3.98 (2H, s), 1.13 (6H, s). The crude product was purified by silica gel column chromatography (9:1 hexane/ethyl acetate). (3.0 g, yield = 88%)

(4R,5R)-(–)-2,2-Dimethyl-α,α,α',α'-tetra(pentafluorophenyl)-1,3-dioxolane-4,5-dimethanol (*R*,*R*)-*TADDOL(C_6F_5)*

^{1}H NMR ($CDCl_3$; 400 MHz): δ 5.42 (2H, s), 3.94 (2H, s), 1.40 (6H, s). The crude product was purified by alumina column chromatography (9:1 hexane/ethyl acetate)}. (0.7 g, yield = 11%)

Characterization

The molecular weight distributions (MWDs) of the polymers were measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH_{HR}-M × 2 (exclusion limit molecular weight = 4×10^6; bead size = 5 μm; column size = 7.8 mm I.D. × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 14 polystyrene standards (Tosoh; M_n = 5.0×10^2–1.09×10^6, $M_w/M_n < 1.2$). NMR spectra were recorded using JEOL JNM-ECA 500 (500.16 MHz for ^{1}H) and JEOL JNM-ECS 400 (399.78 MHz for ^{1}H and 100.53 MHz for ^{13}C) spectrometers.

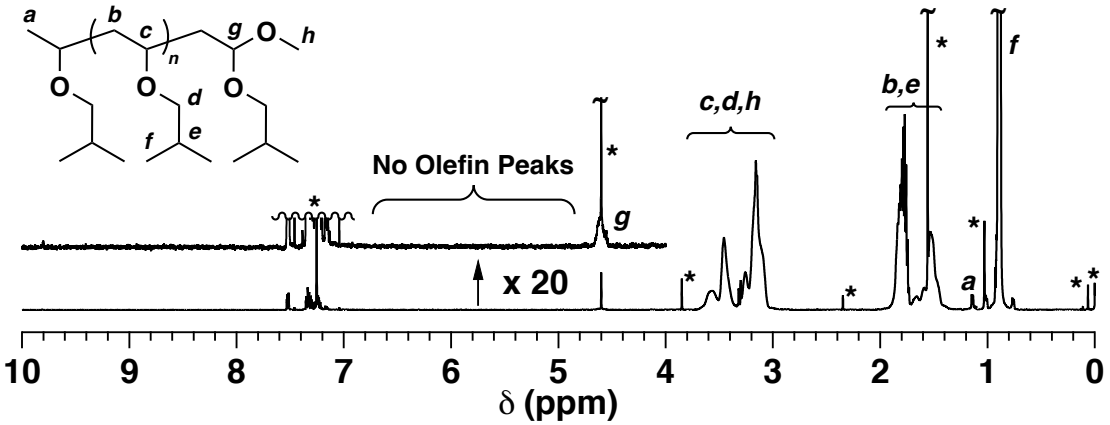


Figure S1. ^{1}H NMR spectrum of the poly(IBVE) obtained by the H-TADDOL/$TiCl_4$ initiating system at 0 ºC (conversion ~ 100%) {$[IBVE]_0$ = 0.76 M, $[H\text{-}TADDOL]_0$ = 5.5 mM, $[TiCl_4]_0$ = 5.0 mM, in hexane/toluene (9/1 v/v)}. * Ligand, toluene, water, grease, and TMS.

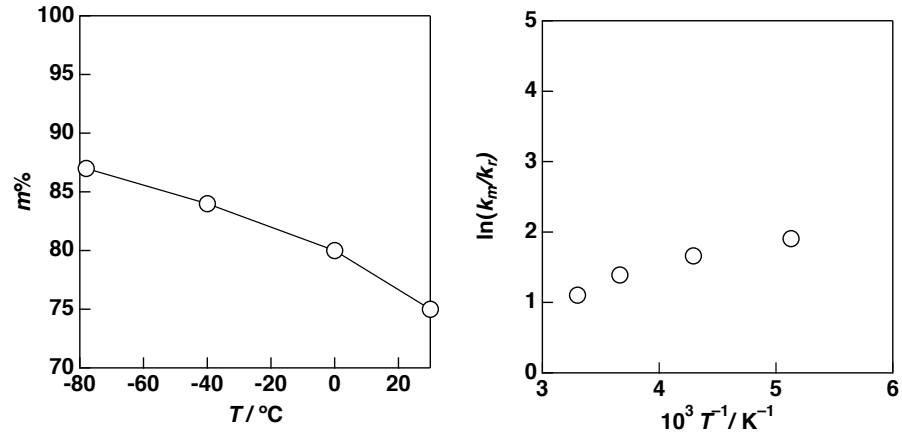


Figure S2. Relation between polymerization temperature and stereoregularity of the resultant poly(IBVE)s obtained by the H-TADDOL/$TiCl_4$ initiating system at various temperatures {$[IBVE]_0$ = 0.76 M, $[H\text{-}TADDOL]_0$ = 5.5 mM, $[TiCl_4]_0$ = 5.0 mM, in hexane/toluene (9/1 v/v)}.

Table S1. Cationic polymerization of IBVE with the H-TADDOL/$TiCl_4$ initiating system using various additives at –78 °C.[a]

entry	$[IBVE]_0$	additive	$[additive]_0$	solvent (v/v)	time	conv. (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	*m* (%)
1	0.76 M	None	–	hexane/toluene (9/1)	30 s	~100	60.5	6.67	87
2			–	toluene	30 s	96	31.3	10.5	85
3	0.10 M		–	hexane/toluene (9/1)	1 min	~100	84.9	2.63	90
4			–	toluene	1 min	83	167	2.05	87
5	0.76 M	EtOAc	50 mM	hexane/toluene (9/1)	15 d	~0	–	–	–
6			20 mM	hexane/toluene (9/1)	15 d	~0	–	–	–
7			20 mM	toluene	60 d	7	–	–	–
8	0.10 M		10 mM	hexane/toluene (9/1)	70 h	58	23.7	2.59	86
9			10 mM	toluene	69 h	75	28.9	1.90	86
10			5.0 mM	hexane/toluene (9/1)	3 h	~100	101	2.52	89
11			5.0 mM	toluene	2 h	~100	51.3	3.10	87
12	0.10 M	THF	5.0 mM	hexane/toluene (9/1)	2 h	~100	32.0	5.14	89
13	0.76 M	DMAc	2.5 mM	hexane/toluene (9/1)	5 min	15	228	1.93	85
14			2.5 mM	toluene	30 min	95	67.8	2.01	85
15			4.0 mM	toluene	2 h	11	32.3	2.47	85
16	0.76 M	DEA	1.0 mM	toluene	12 min	94	81.3	3.67	84
17			2.5 mM	toluene	24 h	4	–	–	–

[a] $[H\text{-}TADDOL]_0$ = 5.5 mM, $[TiCl_4]_0$ = 5.0 mM (DMAc: *N*,*N*-dimethyl acetoamide, DEA: *N*,*N*-diethylaniline). [b] Calculated with polystyrene standards.

Table S2. Cationic polymerization of IBVE with TADDOLs at –78 °C.[a]

entry	TADDOL	$[IBVE]_0$	solvent (v/v)	time	conv. (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	*m* (%)
1	CF_3-TADDOL	0.10 M	hexane/toluene (9/1)	30 s	~100	7.3	1.81	83
2[c]		0.10 M	hexane/toluene (9/1)	30 min	~100	66.2	1.40	90
3[d]		0.10 M	hexane/toluene (9/1)	48 h	68	136	2.05	78
4[c]		0.76 M	hexane/toluene (9/1)	1 min	~100	466	1.67	85
5		0.10 M	toluene	30 s	~100	7.7	1.45	84
6	H-TADDOL	0.10 M	toluene	1 min	83	167	2.05	87
7	*t*Bu-TADDOL	0.10 M	toluene	1 h	~100	25.3	14.8	77
8	$(CF_3)_2$-TADDOL	0.10 M	hexane/toluene (9/1)	30 s	88	6.8	1.80	74
9[c]		0.10 M	hexane/toluene (9/1)	10 min	100	31.1	1.58	76

[a] $[TADDOL]_0$ = 5.5 mM, $[TiCl_4]_0$ = 5.0 mM. [b] Calculated with polystyrene standards. [c] Ethyl acetate (5.0 mM) was added. [d] Ethyl acetate (10 mM) was added.

Table S3. Cationic polymerization of EVE with TADDOLs at –78 °C.[a]

entry	TADDOL	$[EVE]_0$	solvent (v/v)	time	conv. (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	*m* (%)
1	H-TADDOL	0.20 M	hexane/toluene (9/1)	4 h	~100	15.2	2.68	75
2	*t*Bu-TADDOL	0.10 M	hexane/toluene (9/1)	4 h	50	18.2	2.78	81
3	CF_3-TADDOL	0.10 M	hexane/toluene (9/1)	5 min	~100	5.5	2.39	83

[a] $[TADDOL]_0$ = 5.5 mM, $[TiCl_4]_0$ = 5.0 mM. [b] Calculated with polystyrene standards.

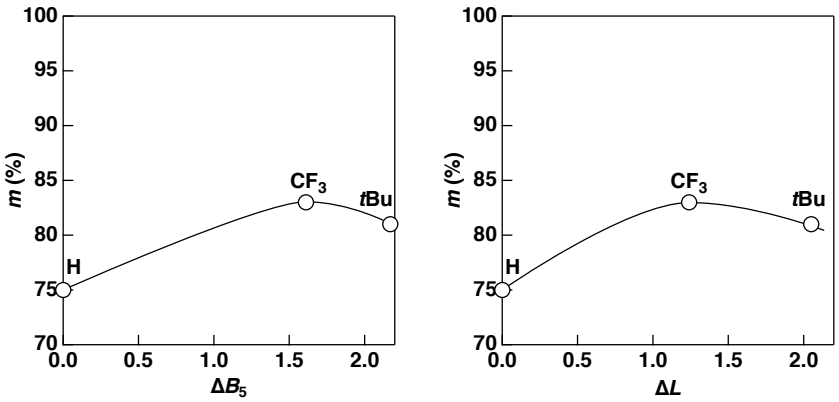
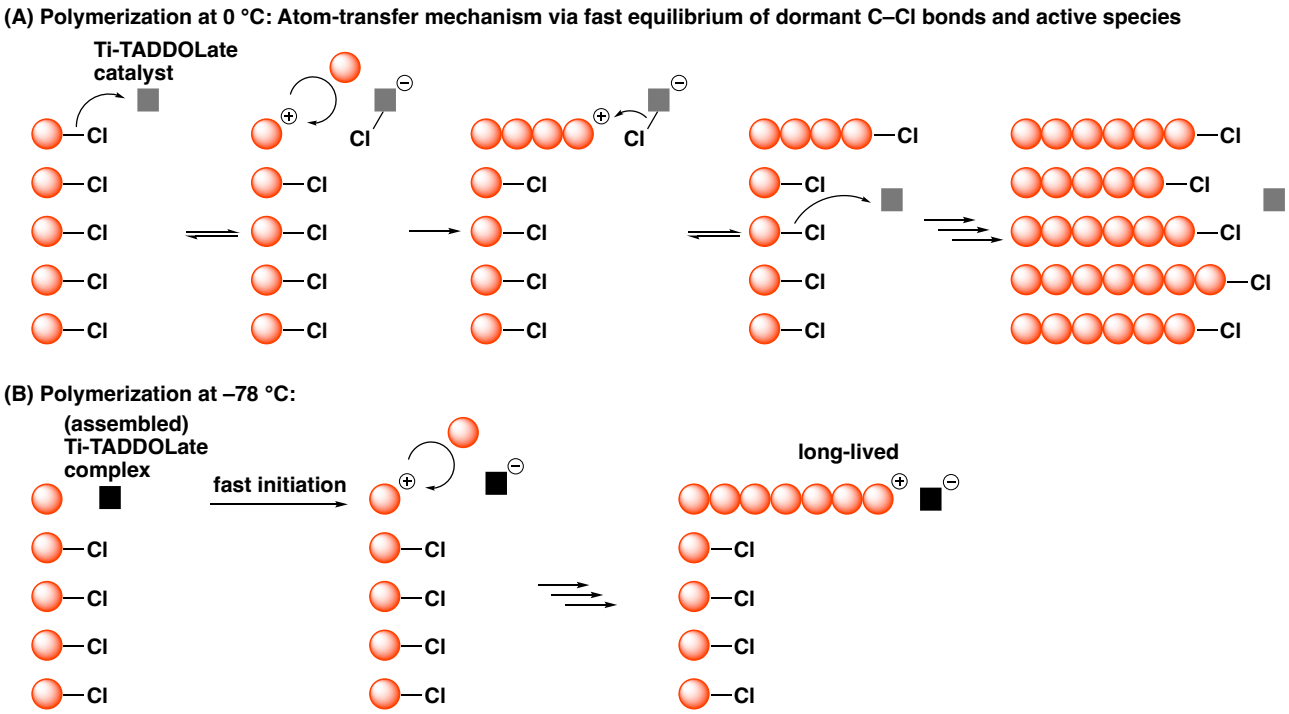


Figure S3. Effects of the bulkiness of the Ar groups in TADDOL on the tacticity of the poly(EVE)s obtained at –78 °C (H, CF_3 and *t*Bu from left to right) {$[EVE]_0$ = 0.10 or 0.20 M, $[TADDOL]_0$ = 5.5 mM, $[TiCl_4]_0$ = 5.0 mM}. The data correspond to Table S2.

Scheme S1. Schematic illustration of polymerization at 0 °C and –78 °C



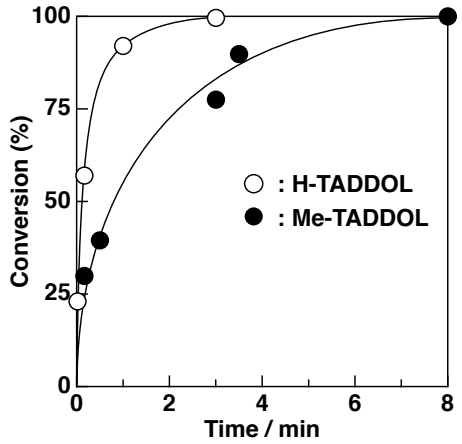


Figure S4. Time−conversion curves for the polymerization with H- or Me-TADDOL at 0 ºC {$[IBVE]_0$ = 0.76 M, $[H\text{-}TADDOL]_0$ = 4.4 mM (for A), $[(R,R)\text{-}Me\text{-}TADDOL]_0$ = 4.0 mM (for B), $[TiCl_4]_0$ = 4.0 mM, in hexane/toluene (9/1 v/v) at 0 ºC}.

Table S4. Cationic polymerization of IBVE with H-TADDOL under various polymerization conditions.[a]

entry	solvent (v/v)	temp. (ºC)	time	conv. (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n [c]	*m* (%)
1	hexane/toluene (9/1)	–40	10 s	~100	13.6	3.26	84
2		0	10 s	65	6.1	1.37	–
			1min	~100	8.1	1.24	80
3		30	1 min	85	6.7	1.23	75
4	toluene	0	5 min	47	5.6	2.33	–
5	CH_2Cl_2	0	1 min	8	–	–	–
6			2 h	~100	5.8	1.20	64

[a] $[IBVE]_0$ = 0.76 M, $[H\text{-}TADDOL]_0$ = 5.5 mM, $[TiCl_4]_0$ = 5.0 mM. [b] Calculated with polystyrene standards.