Electronic Supplementary Information for:

Stereoselective Cationic Polymerization of Vinyl Ethers by Easily and Finely Tunable Titanium Complexes Prepared from Tartrate-Derived Diols: Isospecific Polymerization and Recognition of Chiral Side Chains

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Osaka 560-0043, Japan.

Contents:

Experimental Section

Experimental Section

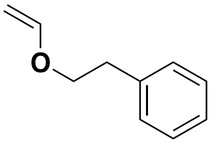
Materials

Isobutyl vinyl ether (IBVE) (TCI; >99.0%), *n*-propyl vinyl ether (*n*-PrVE) (TCI; >97.0%), ethyl vinyl ether (EVE) (TCI; >98.0%), *n*-butyl vinyl ether (*n*-BuVE) (TCI; >98.0%), cyclohexylmethyl vinyl ether (CMVE) (Maruzen Petrochemicals) and *t*-butyl vinyl ether (*t*-BuVE) (Aldrich; ≥98.0%) were washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. (*R*,*R*)- and (*S*,*S*)-*α,α,α',α'*-tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) ($R^1 = R^2$ = Me, Ar = Ph) (TCI; > 97.0%), (*R*,*R*)-TADDOL (R^1 = Me, R^2=Ph, Ar = Ph) (TCI; > 95.0%), (*S*,*S*)-TADDOL (R^1, R^2 = -$(CH_2)_5$-, Ar = Ph) (Daicel; ≥ 98.0%), (*S*,*S*)-TADDOL ($R^1 = R^2$ = Me, Ar = 1-naphthyl) (Aldrich; 99.0%), and (*R*,*R*)-TADDOL ($R^1 = R^2$ = Me, Ar = 2-naphthyl) (Aldrich; ≥ 99.0%) were used without further purification. Commercially obtained $TiCl_4$ (Aldrich; 1.0 M solution in toluene), $SnCl_4$ (Aldrich; 1.0 M solution in heptane), $ZrCl_4$ (Aldrich; 99.99%), $EtAlCl_2$ (Wako; 1.0 M solution in hexane), and $MoCl_5$ (Aldrich; 99.99%) were used without further purification. A stock solution of $NbCl_5$ in a mixture of dichloromethane and ethyl acetate was prepared from commercial anhydrous $NbCl_5$ (Strem; 99.99%). A stock solution of $TaCl_5$ in ethyl acetate was prepared from commercial anhydrous $TaCl_5$ (Strem; >99.99%). 1-(Isobutoxy)ethyl chloride [IBVE–HCl; $CH_3CH(O\textit{i}Bu)Cl$] was prepared via the addition reaction of IBVE with dry HCl, according to the reported method.[S1] Hexane (Wako; 96.0%), toluene (Wako; 99.5%), and dichloromethane (Wako; 99.0%) were dried by passage through solvent purification columns (glass contour). In the syntheses of the monomers, palladium acetate (Aldrich; 98%), 1,10-phenanthroline (Aldrich; ≥99%), EVE (TCI; >98.0%), 2-phenylethanol (Nacalai Tesque; ≥98.0%), (–)-borneol (TCI; >95.0%), (–)-menthol (TCI; >99.0%), (+)-fenchyl alcohol (Aldrich; 96%), methyl L-(–)-lactate (TCI; >98.0%), (*S*)-(–)-2-methyl-1-butanol (TCI; >98.0%), (*S*)-(+)-3-octanol (Aldrich; 97%), and (*R*)-1-[3,5-bis(trifluoromethyl)phenyl]ethanol (TCI; >98.0%) were used without further purification.

Procedure for the Synthesis of Vinyl Ethers

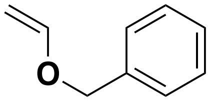
2-Phenylethyl vinyl ether (2-PhEtVE), benzyl vinyl ether (BnVE), bornyl vinyl ether, menthyl vinyl ether, fenchyl vinyl ether, methyl (*S*)-2-(vinyloxy)propanoate, (*S*)-2-methylbutyl vinyl ether (MeBuVE), (*S*)-3-octyl vinyl ether (3-OcVE), and (*R*)-1-[3,5-bis(trifluoromethyl)phenyl]ethyl vinyl ether ([$(CF_3)_2$Ph]EtVE) were synthesized via the transvinylation of the corresponding alcohols [2-phenylethanol, benzyl alcohol, (–)-borneol, (–)-menthol, (+)-fenchyl alcohol, methyl L-(–)-lactate, (*S*)-(–)-2-methyl-1-butanol, (*S*)-(+)-3-octanol, and (*R*)-1-{3,5-bis(trifluoromethyl)phenyl}ethanol, respectively] using $Pd(OAc)_2$ according to the reported method.[S2] The typical synthesis procedure is as follows. $Pd(OAc)_2$ (0.465 g = 2.07 mmol = 1 mol% with respect to 2-phenyl ethanol) and 1,10-phenanthroline (0.448 g = 2.49 mmol) were dissolved in 140 mL of ethyl vinyl ether (1.45 mol). 2-Phenylethanol (25.3 g = 0.207 mol) was added to the solution, and the flask was stirred at 55 °C for 11 h (conversion: 80% by NMR). The crude product was purified by column chromatography (silica gel, dichloromethane) and distilled twice over calcium hydride before use.

2-Phenyl Ethyl vinyl ether (2-PhEtVE)



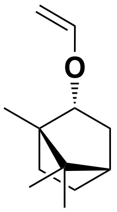
^{1}H NMR (CDCl$_3$; 400MHz): δ 7.34-7.20 (5H, m), 6.46 (1H, dd), 4.19 (1H, dd), 4.00 (1H, dd), 3.90 (2H, t), 2.98 (2H, t).

Benzyl vinyl ether (BnVE)



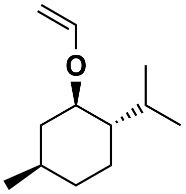
^{1}H NMR (CDCl$_3$; 400MHz): δ 7.43-7.26 (5H, m), 6.56 (1H, dd), 4.76 (1H, s), 4.30 (1H, dd), 4.08 (1H, dd).

(1S,2R,4S)-Bornyl vinyl ether



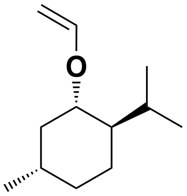
^{1}H NMR (CDCl$_3$; 400MHz): δ 6.39 (1H, dd), 4.11 (1H, dd), 4.0 (1H, m), 3.93 (1H, dd), 2.27–2.17 (1H, m), 2.04–1.95 (1H, m), 1.78–1.64 (2H, m), 1.32–1.18 (2H, m), 1.11–1.01 (1H, dd), 0.88 (9H, t).

(1S,2R,4R)-Menthyl vinyl ether



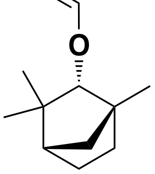
^{1}H NMR (CDCl$_3$; 400MHz): δ 6.31 (1H, dd), 4.27 (1H, dd), 3.93 (1H, dd), 3.51 (1H, dt), 2.17-2.02 (2H, m), 1.71–1.62 (2H, m), 1.47–1.29 (2H, m), 1.07–0.73 (12H, m).

(1R,2S,4S)-Menthyl vinyl ether



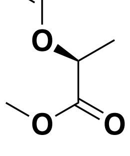
^{1}H NMR (CDCl$_3$; 400MHz): δ 6.31 (1H, dd), 4.27 (1H, dd), 3.93 (1H, dd), 3.51 (1H, dt), 2.17-2.02 (2H, m), 1.71–1.62 (2H, m), 1.47–1.29 (2H, m), 1.07–0.73 (12H, m).

(1R,2R,4S)-Fenchyl vinyl ether



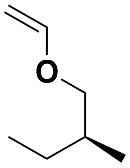
^{1}H NMR (CDCl$_3$; 400MHz): δ 6.31 (1H, dd), 4.24 (1H, dd), 3.88 (1H, dd), 3.34 (1H, d), 1.81-1.64 (3H, m), 1.51–1.35 (2H, m), 1.15–0.95 (8H, m), 0.86 (3H, s).

methyl (S)-2-(vinyloxy)propanoate



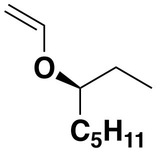
^{1}H NMR (CDCl$_3$; 400MHz): δ 6.18 (1H, dd), 4.35 (1H, q), 4.16 (1H, dd), 4.25 (1H, dd), 3.60 (3H, s), 1.42 (3H, d).

(S)-2-methylbutyl vinyl ether (MeBuVE)



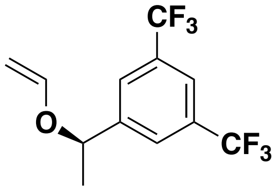
^{1}H NMR (CDCl$_3$; 400MHz): δ 6.36 (1H, dd), 4.14 (1H, dd), 3.94 (1H, dd), 3.58–3.43 (2H, m), 1.71 (1H, m), 1.46 (1H, m), 1.13~1.25 (1H, m), 0.86~0.96 (6H, m).

(S)-3-octyl vinyl ether (3-OcVE)



^{1}H NMR (CDCl$_3$; 400MHz): δ 6.31 (1H, dd), 4.26 (1H, dd), 3.94 (1H, dd), 3.64 (1H, m), 1.22~1.61 (10H, m), 0.90 (6H, m).

(R)-1-[3,5-bis(trifluoromethyl)phenyl]ethyl vinyl ether ([(CF$_3$)$_2$Ph]EtVE)



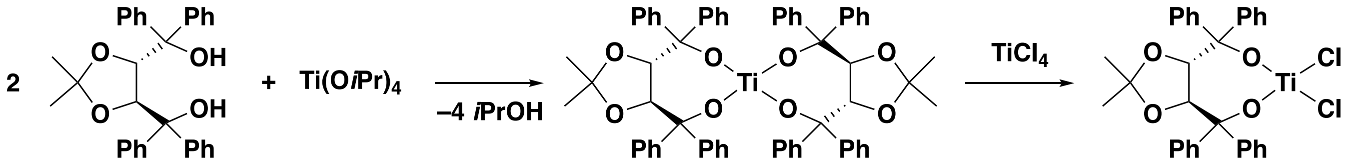
^{1}H NMR (CDCl$_3$; 400MHz): δ 7.80 (1H, s), 8.44 (1H, s), 7.77 (1H, s), 6.33 (1H, dd), 5.02 (1H, q), 4.24 (1H, dd), 4.09 (1H, dd) , 1.56 (3H, d).

Polymerization Procedures

The typical polymerization procedure is as follows. A glass tube equipped with a three-way stopcock and a magnetic stirrer bar was dried using a heat gun (Ishizaki, PJ-206A; blow temperature ~450 °C) under dry nitrogen. Hexane and isobutyl vinyl ether were sequentially added to the tube using dry syringes. In another tube, a TADDOL solution was added to a solution of TiCl$_4$ in toluene, and the mixture was kept at –78 ºC for at least 30 min to achieve quantitative complexation. The polymerization was initiated by adding the Ti-TADDOLate solution to the monomer solution at –78 ºC. After a predetermined time, the reaction was terminated by the addition of methanol containing a small amount of aqueous ammonia. The quenched mixture was washed with water. Then, the volatiles were removed under reduced pressure at 50 °C to yield the polymer. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport B; GL Sciences Inc.) using hexane as an internal standard.

Characterization

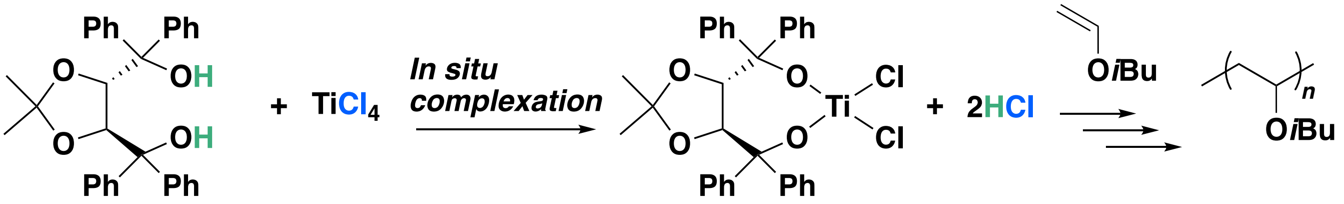
The molecular weight distributions (MWDs) of the polymers were measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH$_{\mathrm{HR}}$-M × 2 (exclusion limit molecular weight = 4×10^6; bead size = 5 μm; column size = 7.8 mm I.D. × 300 mm); flow 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; $M_n = 5.0\times10^2$–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. Differential scanning calorimeter (DSC) was operated using Shimadzu DSC-60 Plus.



(*S*,*S*)-TADDOL ($R^1 = R^2$ = Me, Ar = Ph) (0.840 g = 1.80 mmol) was dissolved in dry toluene (11 mL) and treated with Ti(O*i*Pr)$_4$ (0.283 mL = 0.95 mmol) under dry nitrogen. The suspension was stirred at 40 ºC for 12 h, and heated to reflux temperature for an additional 5 h. The solvent was then evaporated in vacuo, and Ti(TADDOLate)$_2$ was obtained as a slightly yellow solid. The product was stored under dry nitrogen. ^{1}H NMR (CDCl$_3$; 500MHz): δ 7.57-7.54 (m, 8H), 7.42-7.38 (8H, m), 7.27-7.08 (24H, m), 5.03 (4H, s), 0.70 (12H, s).

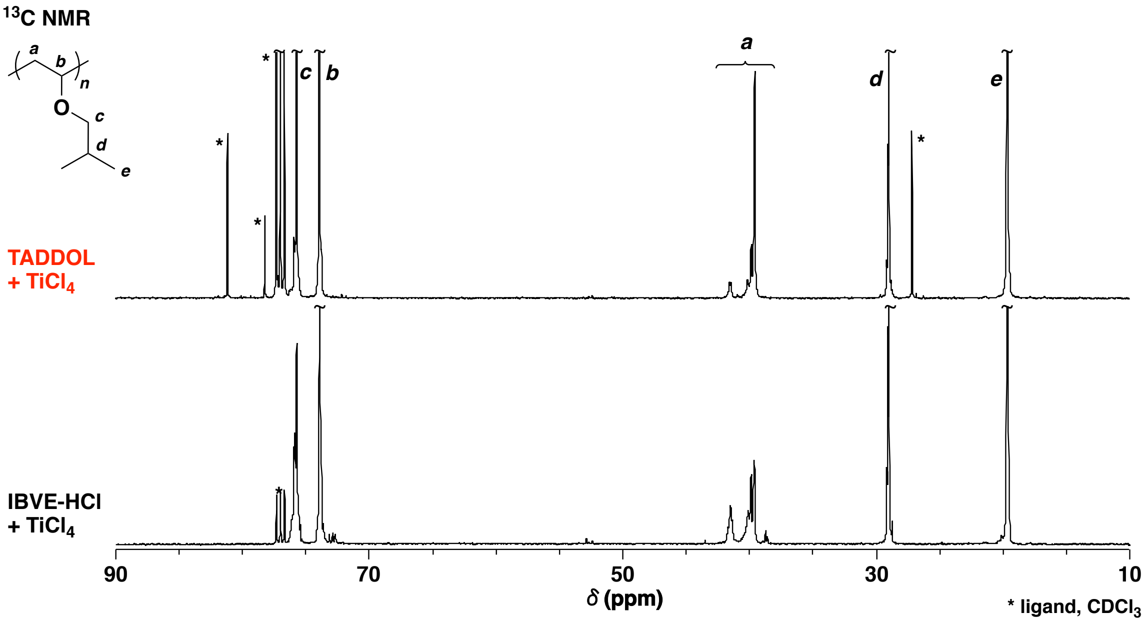
The Ti(TADDOLate)$_2$ was dissolved in dry toluene, and the 100 mM solution of Ti(TADDOLate)$_2$ (1.00 mL) was added to a 33.3 mM TiCl$_4$ solution (3.00 mL in toluene) under dry nitrogen. The mixture solution was stirred at room temperature for 1.5 h, and a yellow Cl$_2$Ti(TADDOLate) solution was obtained.

Scheme S1 Synthesis procedure of Cl$_2$Ti-TADDOLate

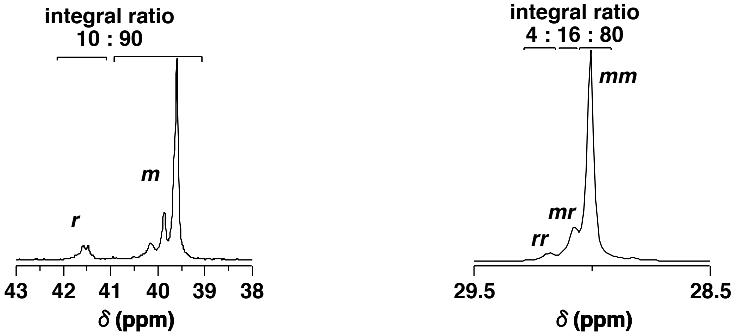


Scheme S2 Polymerization scheme by the simple method mixing TADDOL, TiCl$_4$, and isobutyl VE

(A) Poly(IBVE)



Expanded spectra for the poly(IBVE) (TADDOL + TiCl$_4$)



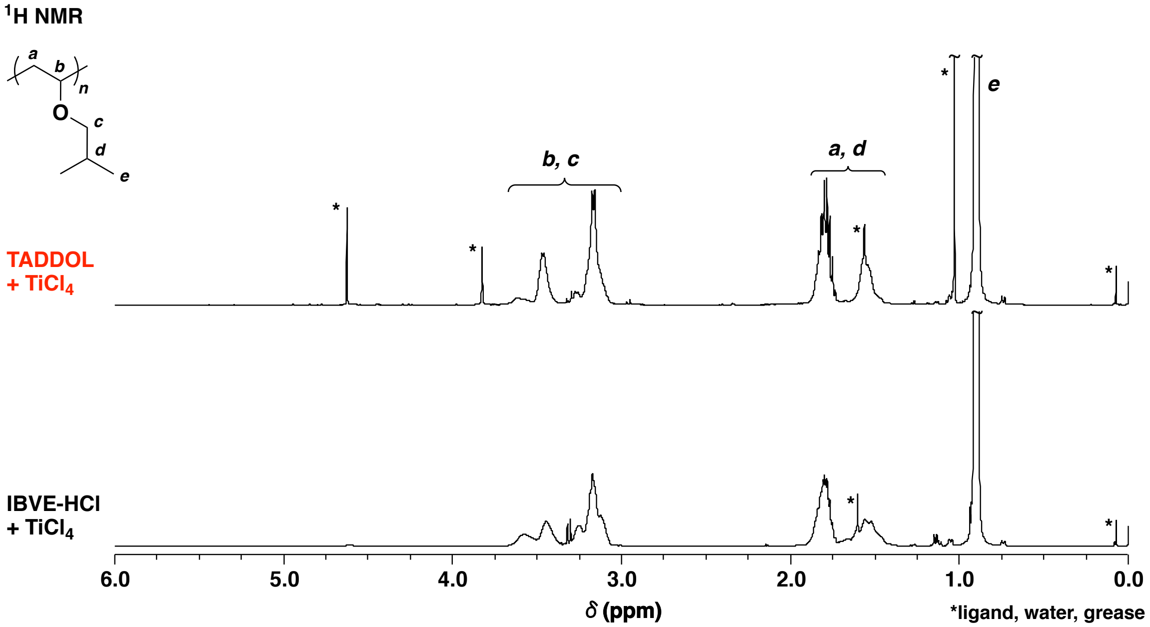
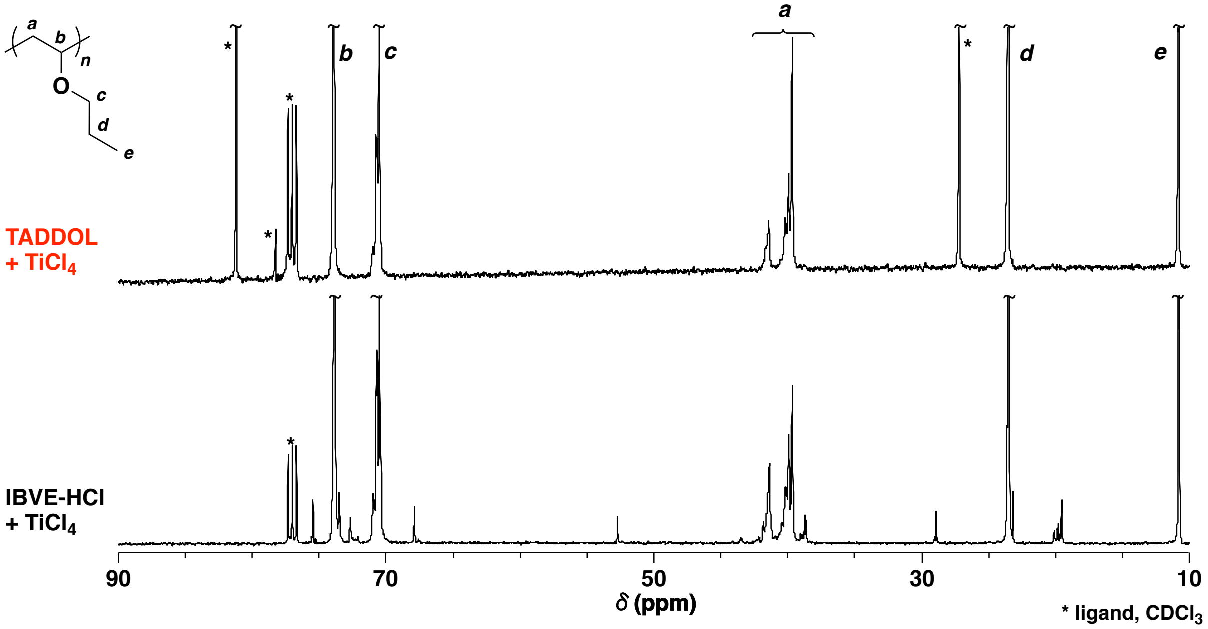


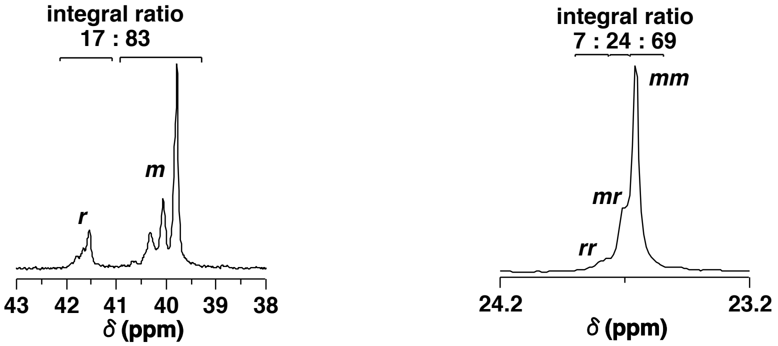
Fig. S1 ^{13}C and ^{1}H NMR spectra of (A) poly(IBVE), (B) poly(*n*-PrVE), and (C) poly(2-PhEtVE); in $CDCl_3$ at 50 ºC (The same samples as those shown in Fig. 2A, 2B, and 2C, respectively; see also Table S2 and S3).

(B) Poly(n-PrVE)

^{13}C NMR



Expanded spectra for the poly(*n*-PrVE) (TADDOL + TiCl$_4$)



^{1}H NMR

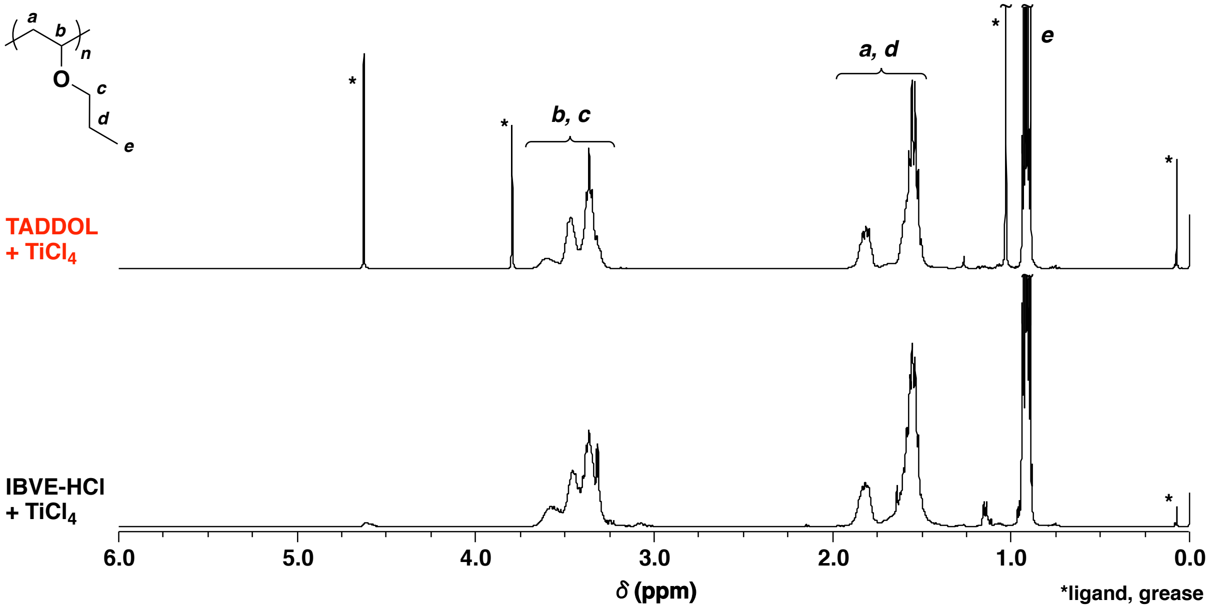
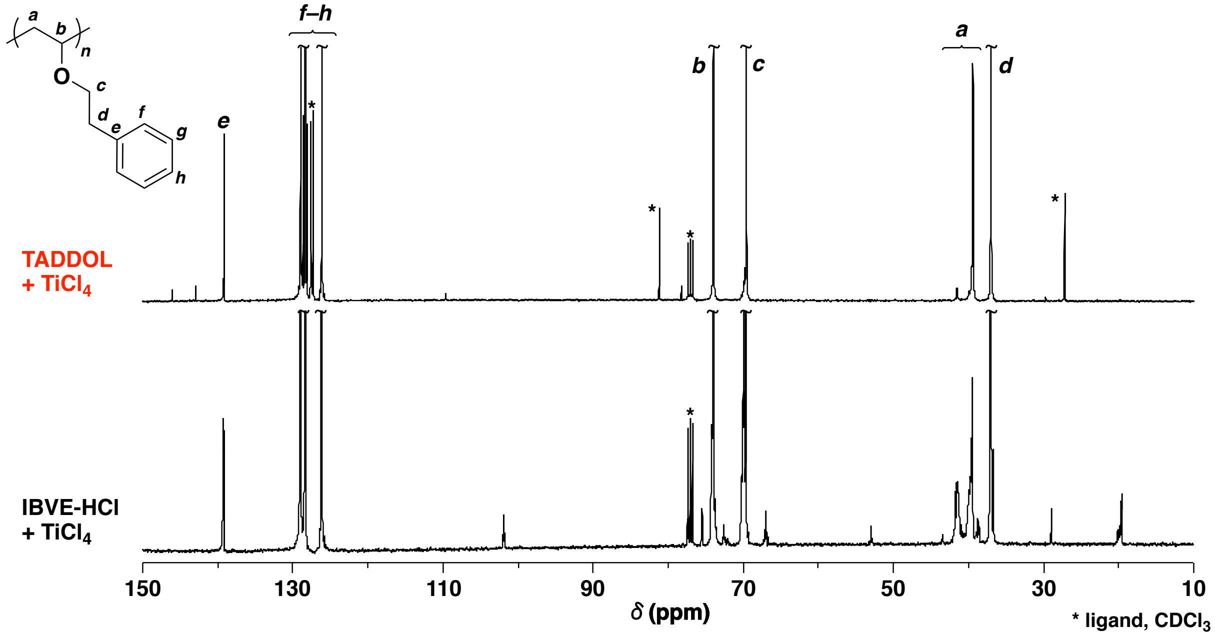


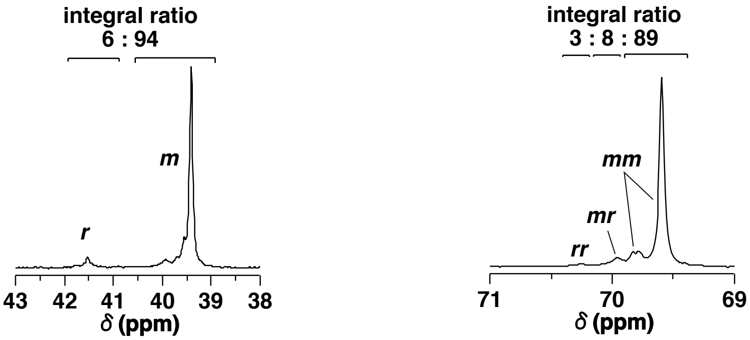
Fig. S1 (*continued*)

(C) Poly(2-PhEtVE)

^{13}C NMR



Expanded spectra for the poly(*n*-PrVE) (TADDOL + TiCl$_4$)



^{1}H NMR

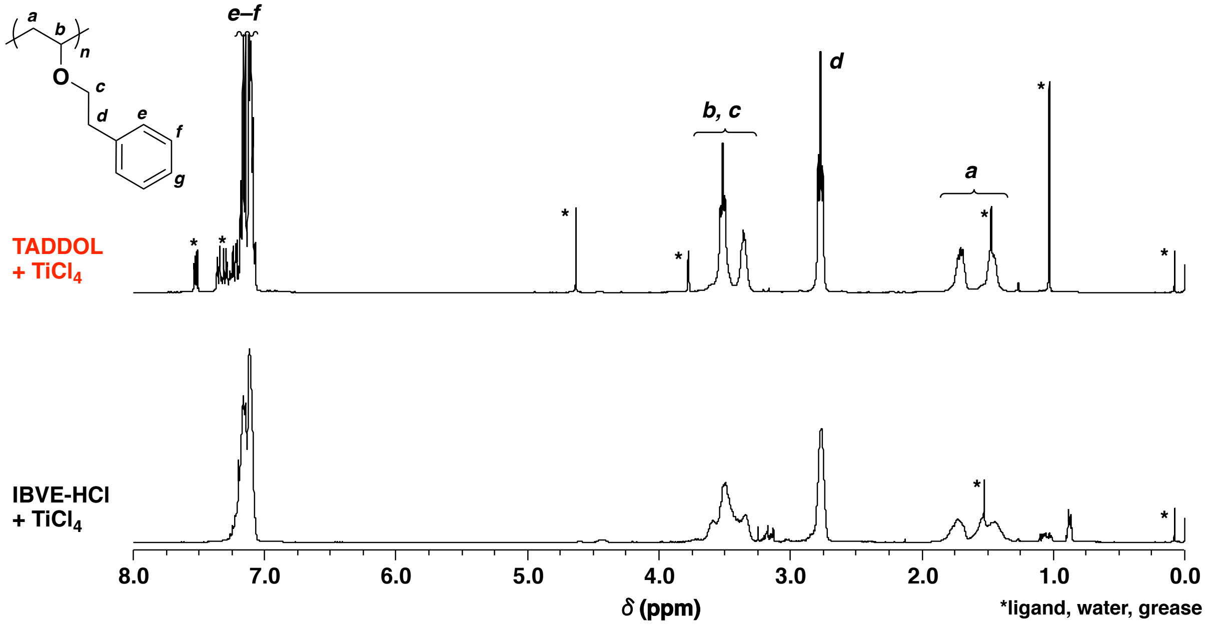


Fig. S1 (*continued*)

Table S1. Cationic polymerization of IBVE using various metal TADDOLates[a]

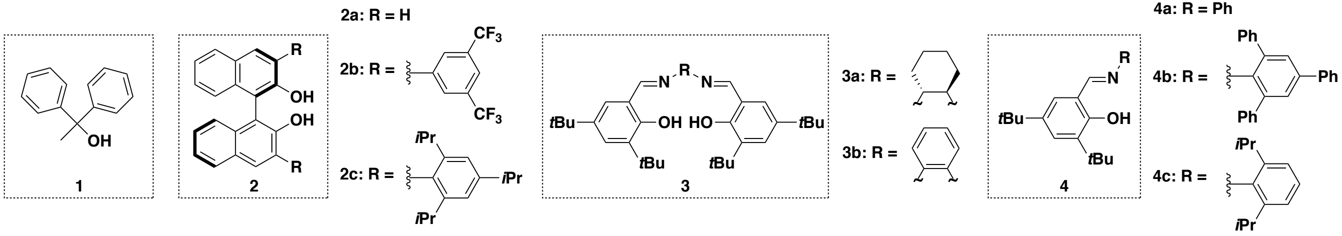
entry	TADDOL structure			metal halide	solvent	time	conv. (%)	M_n×10^{-3} [b]	M_w/M_n [b]	m[c] (%)
	R^1	R^2	Ar							
1	Me	Me	Ph	$TiCl_4$	hexane/toluene (9/1)	30 s	~100	45.4	6.67	87
2				$TiCl_4$	hexane/CH_2Cl_2 (9/1)	30 s	~100	60.5	4.75	87
3				$TiCl_4$	toluene	30 s	96	31.3	10.48	85
4				$TiCl_4$	CH_2Cl_2	30 s	~100	14.9	1.68	81
5				$SnCl_4$	hexane/CH_2Cl_2 (9/1)	30 s	~100	42.4	1.83	78
6				$ZrCl_4$	toluene	480 h	66	16.5	3.74	70
7				$EtAlCl_2$	toluene/CH_2Cl_2 (9/1)	5 min	98	33.1	1.98	76
8[d]				$NbCl_5$	hexane/CH_2Cl_2 (9/1)	4 h	54	25.3	2.19	79
9[e]				$TaCl_5$	toluene/CH_2Cl_2 (9/1)	1 h	95	40.2	2.67	76
10				$MoCl_5$	toluene/CH_2Cl_2 (9/1)	30 s	76	19.6	2.52	70

[a] $[IBVE]_0$ = 0.76 M, $[MCl_n]_0$ = 5.0 mM, $[TADDOL]_0$ = 5.5 mM at –78ºC. [b] Determined by GPC in chloroform on the basis of polystyrene calibration. [c] Calculated by ^{13}C NMR. [d] In the presence of 25 mM of ethyl acetate. [e] In the presence of 250 mM of ethyl acetate.

Note for **Table S1**: The number-average molecular weight and molecular weight distribution were influenced by the polymerization solvents, most likely because of the solubility of the polymer and the catalyst. The catalyst was completely soluble in toluene and CH_2Cl_2, but not in hexane. For fast reactions, exotherm of the polymerization could influence the polymerization control.

Table S2. Cationic polymerization of IBVE using other ligands than TADDOL[a]

<Ligand structures>

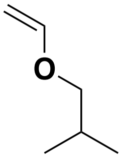


entry	ligand	temp. (ºC)	time	conv. (%)	M_n × 10^{-3} [b]	M_w/M_n [b]	m (%)[c]
1	1	–78	1 min	84	59.1	5.60	79
2	2a	–78	30 s	99	21.2	2.41	73
3	2b	–78	30 s	~100	14.6	2.64	75
4	2c	–78	3 min	~0	–	–	–
5[d,e]	3a	0	72 h	6.4	–	–	–
6[d,f]	3b	0	168 h	12	–	–	–
7[g]	4a	–78	7 h	94	29.9	1.11	59
8[g]	4b	–78	168 h	64	41.6	5.33	74
9[g]	4c	–78	19 h	97	12.3	1.88	72
10	None	–78	5 min	~100	4.6	1.28	71

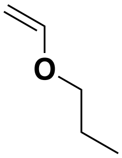
[a] $[IBVE]_0$ = 0.76 M, $[TiCl_4]_0$ = 5.0 mM, $[ligand]_0$ = 11 mM (for entry 1) or 5.0 mM (for entries 2–9) in toluene. [b] Determined by GPC in chloroform on the basis of polystyrene calibration. [c] Calculated by ^{13}C NMR. [d] Results taken from reference S3. [e] In the presence of 0.10 M of ethyl acetate. [f] In the presence of 1.0 M of ethyl acetate. [g] Results taken from reference S4.

Table S3. Cationic polymerization of various VEs using the titanium TADDOLate[a]

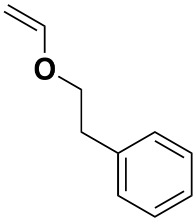
<Monomer structures>



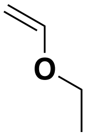
IBVE



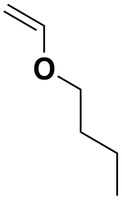
***n*-PrVE**



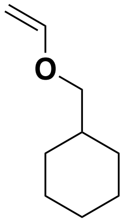
2-PhEtVE



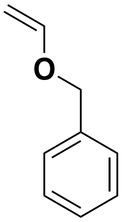
EVE



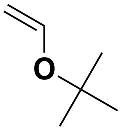
***n*-BuVE**



CMVE



BnVE

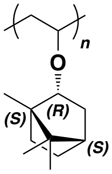
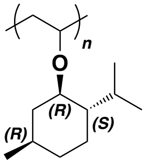
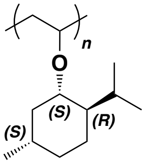


***t*-BuVE**

entry	monomer	[monomer]$_0$	solvent	time	conv. (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	*m* (%)
1	IBVE	0.76 M	hexane/toluene	30 s	~ 100	45.4	6.67	87
2		0.20 M	hexane/toluene	30 s	78	302	1.86	89
3		0.10 M	hexane/toluene	1 min	~100	84.9	2.63	90
4		0.05 M	hexane/toluene	1 min	~100	50.0	2.77	90
5	*n*-PrVE	0.76 M	hexane/toluene	15 min	~100	117	3.60	82
6		0.10 M	hexane/toluene	30 min	69	31.7	5.76	83
7	2-PhEtVE	0.76 M	toluene	5 min	97	214	2.59	87
8		0.10 M	toluene	15 min	~ 100	108	2.58	94
9	EVE	0.76 M	hexane/toluene	5 h	~100	37.4	2.77	75
10	*n*-BuVE	0.76 M	hexane/toluene	5 min	97	113	2.65	79
11		0.10 M	hexane/toluene	10 min	42	62.0	3.59	82
12	CMVE	0.76 M	hexane/toluene	1 min	56	121	3.15	78
13	BnVE	0.76 M	toluene	15 min	59	49.2	3.87	70
14	*t*-BuVE	0.76 M	hexane/toluene	30 sec	~100	15.2	4.92	68[c]

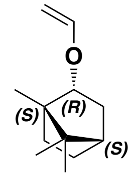
[a] $[TiCl_4]_0$ = 5.0 mM, [TADDOL ($R^1 = R^2$ = Me, Ar = Ph)]$_0$ = 5.5 mM in hexane/toluene (9/1 v/v) or toluene at –78 ºC. [b] Determined by GPC in chloroform on the basis of polystyrene calibration. [c] Calculated from triad values.

Table S4. Solubility of polymers (1 wt%) synthesized from chiral VEs using the chiral titanium TADDOLates

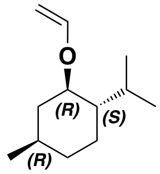
	 **Poly{(1*S*,2*R*,4*S*)-bornyl VE}**		 **Poly{(1*S*,2*R*,4*R*)-menthyl VE}**		 **Poly{(1*R*,2*S*,4*S*)-menthyl VE}**	
	(*R*,*R*)-TADDOL	(*S*,*S*)-TADDOL	(*R*,*R*)-TADDOL	(*S*,*S*)-TADDOL	(*R*,*R*)-TADDOL	(*S*,*S*)-TADDOL
Chloroform	Soluble	Insoluble[a]	Insoluble	Soluble	Soluble	Insoluble
Dichloromethane	Soluble	Insoluble	Insoluble	Soluble	Soluble	Insoluble
1,1,2,2-Tetrachloroethane	Soluble	Insoluble	Insoluble	Soluble	Soluble	Insoluble
o-Dichlorobenzene	Soluble	Insoluble	Insoluble	Soluble	Soluble	Insoluble
Hexane	Soluble	Insoluble	Insoluble	Soluble	Soluble	Insoluble
Toluene	Soluble	Insoluble	Insoluble	Soluble	Soluble	Insoluble
THF	Soluble	Insoluble	Insoluble	Soluble	Soluble	Insoluble

[a] Soluble at a very low concentration.

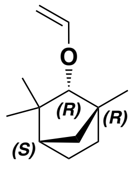
Table S5. Cationic polymerization of chiral VEs using the titanium TADDOLate[a]



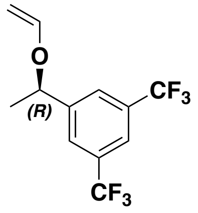
(1*S*,2*R*,4*S*)-bornyl VE



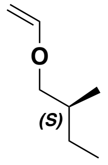
(1*S*,2*R*,4*R*)-menthyl VE



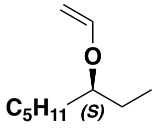
(1*R*,2*R*,4*S*)-fenchyl VE



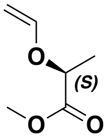
(*R*)-1-[(CF$_3$)$_2$Ph]EtVE



(*S*)-2-MeBuVE



(*S*)-3-OcVE



Me-(*S*)-2-(vinyloxy) propanoate

entry	monomer	TADDOL chirality	[monomer]$_0$	time	conv. (%)	M_n × 10^{-3} [b]	M_w/M_n [b]
1	(1*S*,2*R*,4*S*)-bornyl VE	(*S*,*S*)	0.51 M	5 min	79	128	2.06
2		(*R*,*R*)		2 min	82	30.5	3.38
3	(1*S*,2*R*,4*R*)-menthyl VE	(*S*,*S*)	0.46 M	1 min	~100	55.8	2.38
4		(*R*,*R*)		1 min	~100	–[c]	–[c]
5	(1*R*,2*R*,4*S*)-fenchyl VE	(*S*,*S*)	0.51 M	5 min	~100	48.1	1.59
6		(*R*,*R*)		5 min	56	30.4	2.39
7	(*R*)-1-[(CF$_3$)$_2$Ph]EtVE	(*S*,*S*)	0.46 M	4 h	~50	3.7	1.15
8		(*R*,*R*)		4 h	~50	3.8	1.15
9	(*S*)-2-MeBuVE	(*S*,*S*)	0.67 M	30s	48	25.4	2.81
10		(*R*,*R*)		30 s	66	18.9	3.60
11	(*S*)-3-OcVE	(*S*,*S*)	0.50 M	30 s	79	8.7	2.66
12		(*R*,*R*)		30 s	89	11.0	2.46
13	Me-(*S*)-2-(vinyloxy) propanoate	(*S*,*S*)	0.75 M	44 h	~0	–	–
14		(*R*,*R*)		44 h	~0	–	–

[a] [TiCl$_4$]$_0$ = 5.0 mM, [TADDOL (R^1 = R^2 = Me, Ar = Ph)]$_0$ = 5.5 mM in hexane/CH$_2$Cl$_2$ (9/1 v/v) at –78 ºC. [b] Determined by GPC in chloroform on the basis of polystyrene calibration. [c] The polymer was insoluble in chloroform.

(A) Poly[(1S,2R,4S)-bornyl VE]

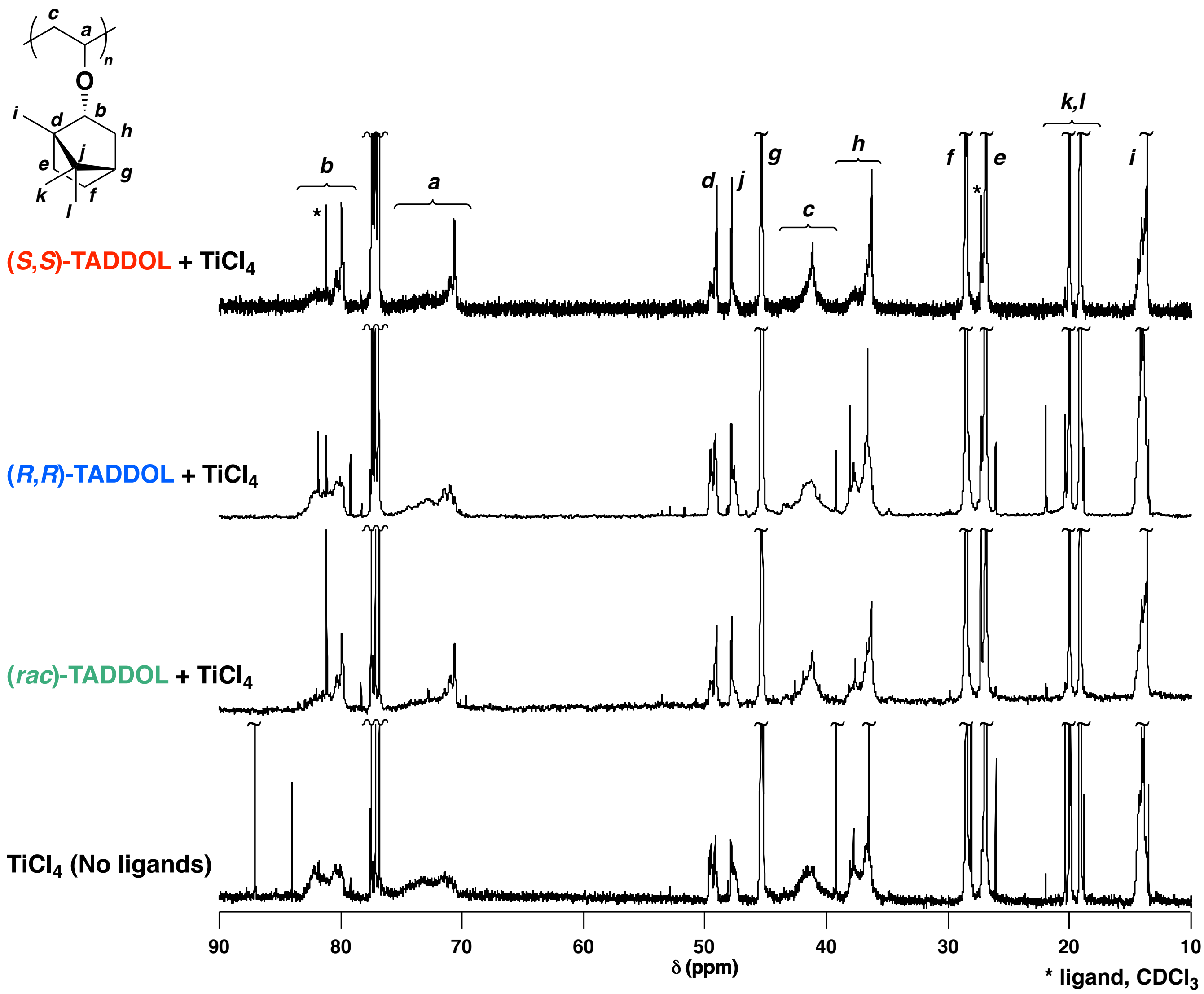
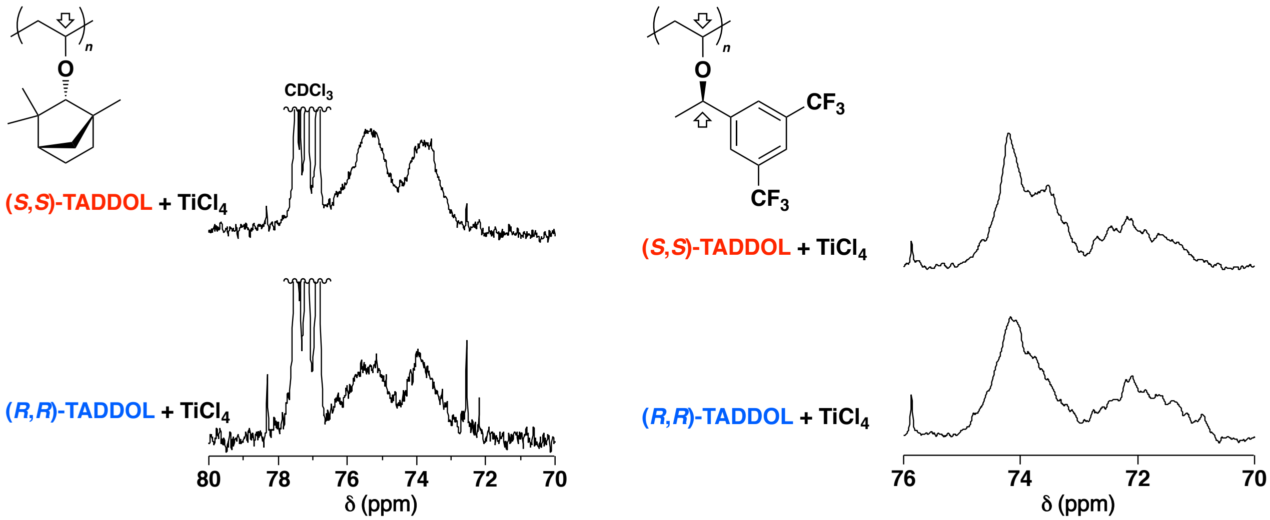


Fig. S2 ^{13}C NMR spectra of poly(chiral VE)s synthesized by $TiCl_4$ with (*S*,*S*)- or (*R*,*R*) TADDOL; in $CDCl_3$ (for A, B, and C), $C_2D_2Cl_4$ (for D) or CD_2Cl_2 (for E) at 30 ºC (The same samples as those shown in Fig. 3 and Table S5).

(B) Poly[(1R,2R,4S)-fenchyl VE] *(C) Poly[(R)-1-{3,5-bis(trifluoromethyl)phenyl}ethyl VE]*



(D) Poly[(S)-2-methylbutyl VE] *(E)Poly[(S)-3-octyl VE]*

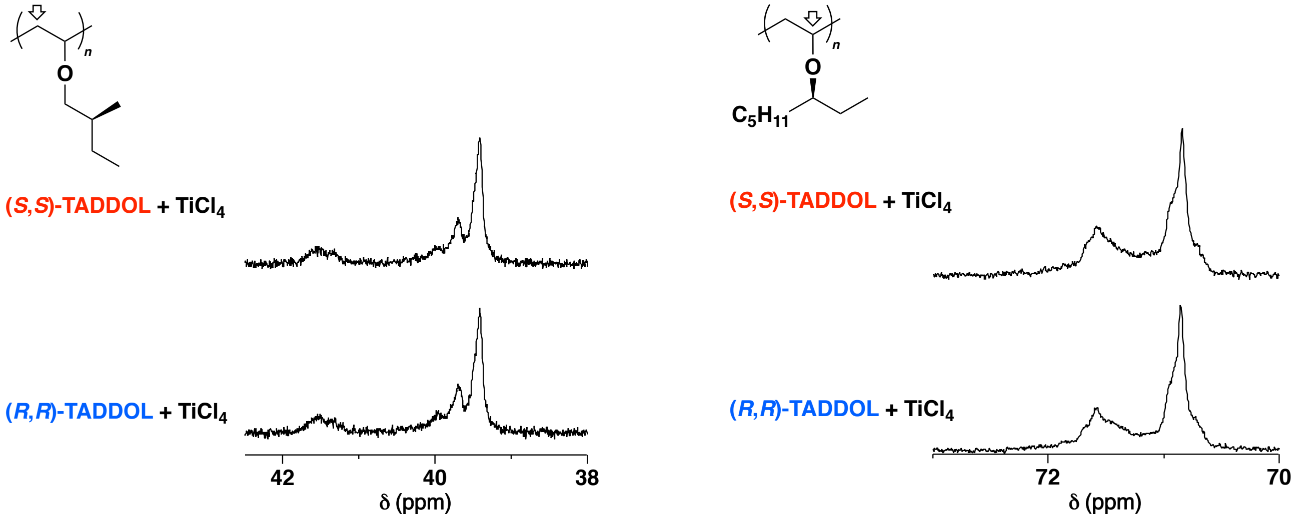
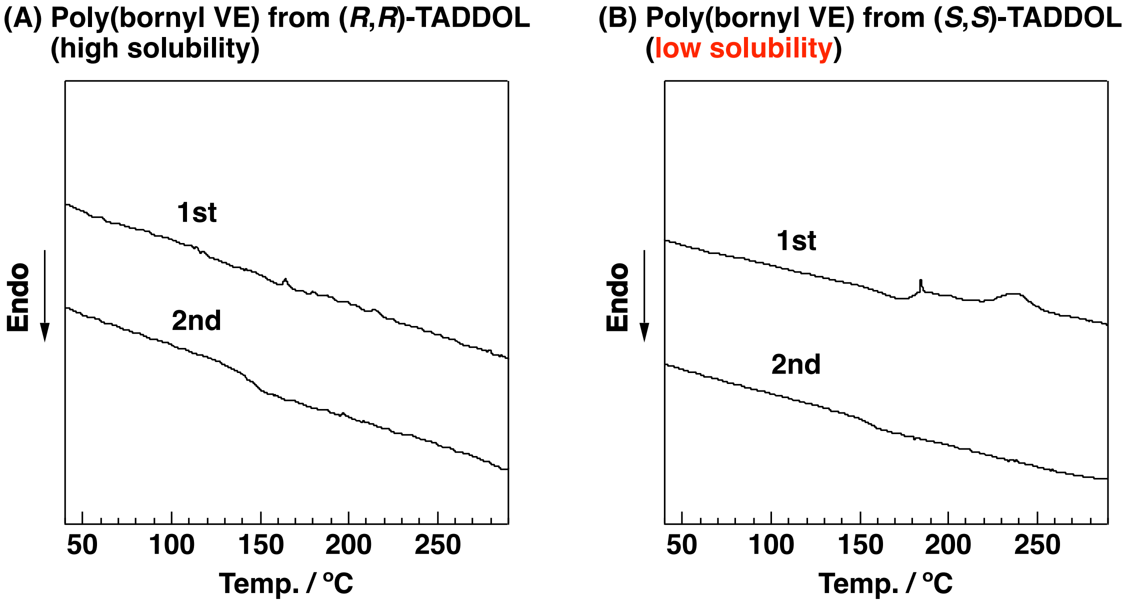
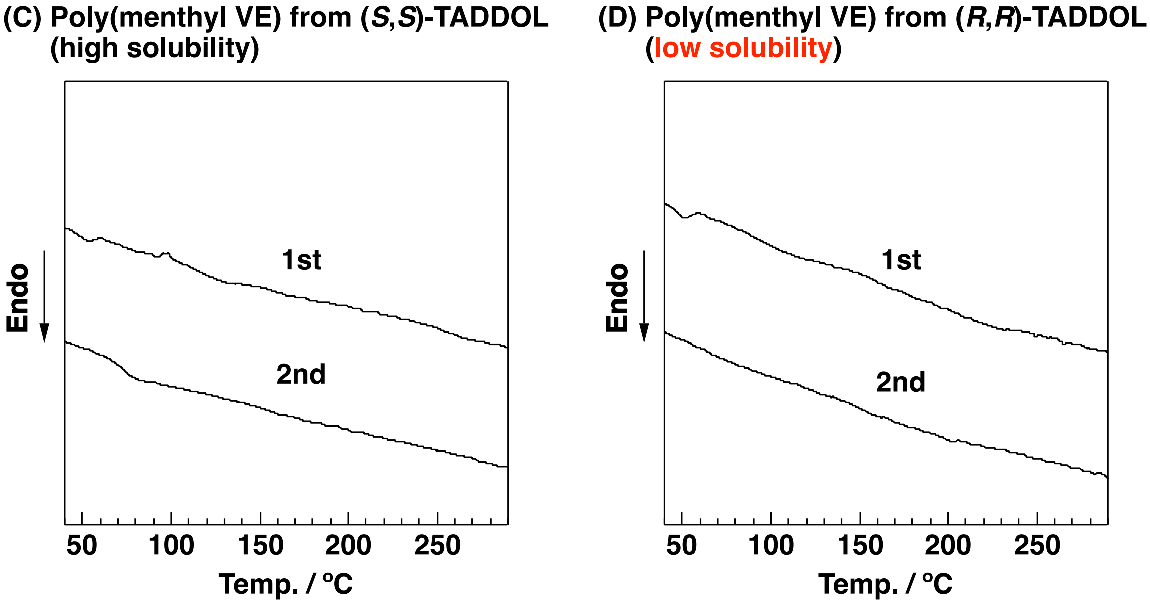


Fig. S2 *(continued)*

Note for **Fig. S2:** The titanium TADDOLate catalyst did not likely recognize chirality in small pendant groups such as those of 2-methylbutyl VE and 3-octyl VE (D and E). Appropriate bulky chiral pendant groups are most likely needed to this "chiral recognition" phenomenon under the examined conditions. Methine carbon signals were shown for polymers of secondary alkyl VEs (A–C and E), while methylene carbon signals were shown for a primary alkyl VE (D). This is because the methylene carbon signals of secondary VEs were broad and thus not suitable for analysis of tacticity.



Poly (bornyl VE) from (*S*,*S*)-TADDOL showed exothermic signals after T_g (~ 160 ºC) on the 1st scan, while the counterpart from (*R*,*R*)-TADDOL did not. These exothermic signals are most likely assigned to T_c. However, T_m was difficult to observe because the value was estimated[S5] to be over the degradation temperature.



From the 2nd scan, poly(menthyl VE) from (*R*,*R*)-TADDOL appeared to have T_g around 200 ºC, while poly(menthyl VE) from (*S*,*S*)-TADDOL clearly showed T_g around 80 ºC. T_m was difficult to observe because of the same reason as poly(bornyl VE)s.

Fig. S3 DSC profiles (1st and 2nd heating scan) of poly(bornyl VE)s (A and B) and poly(menthyl VE)s (C and D). The heating and cooling rates were 10 °C min^{-1} in the range from 30 to 300 ºC.

Chain-end model is represented by Bernoullian statistics, and the triad distribution can be described by a single value of σ_1, the probability that a new monomer will react with a growing chain end to give the same configuration as that of the last unit on the chain[S6]:

$$(mm) = \sigma_1^2$$

$$(mr) = 2(\sigma_1 - \sigma_1^2)$$

$$(rr) = (1 - \sigma_1)^2$$

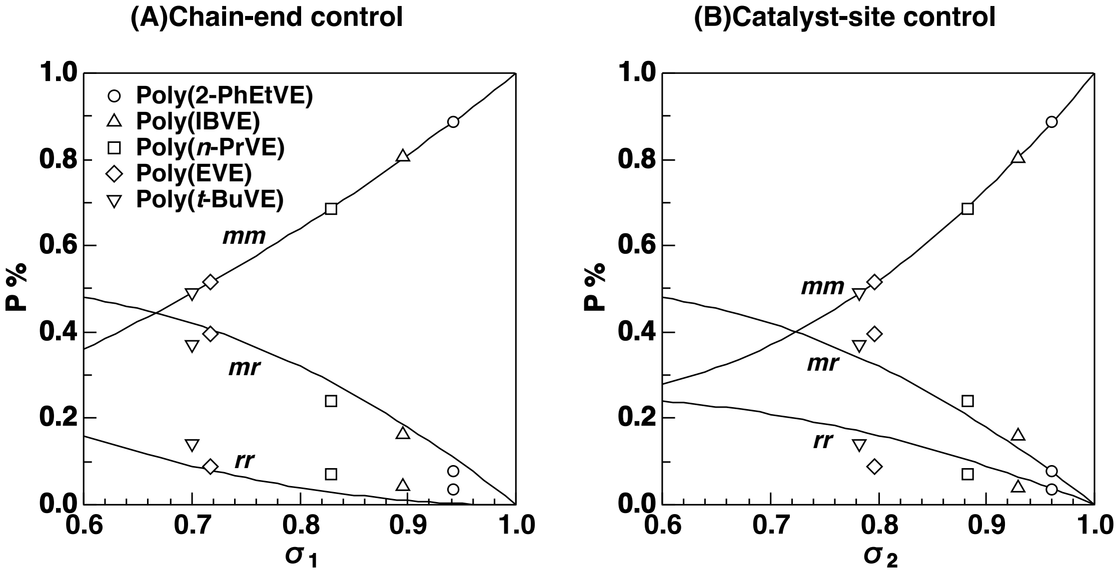
In catalyst-site control model, the triad distribution can be described by a parameter σ_2, the probability of forming a (*S*) [or (*R*)] unit at the (*S*)- [or (*R*)-] selective site[S7]:

$$(mm) = 1 - 3(\sigma_2 - \sigma_2^2)$$

$$(mr) = 2(\sigma_2 - \sigma_2^2)$$

$$(rr) = \sigma_2 - \sigma_2^2$$

These relationships are plotted in the following figures for the poly(VE)s obtained by TADDOL/$TiCl_4$ system ("P" is the probability of the each triad).



Even though the statistics for the highly isotactic polymers are closer to the theoretical values of catalyst-site control, we need more detailed investigation to determine the exact mechanism of the stereoregulation.

The ratios of the triads of the obtained polymers calculated from ^{13}C NMR analyses are in the following Table. $4(mm)(rr)/(mr)^2$ and $(mr)/2(rr)$ should be 1 if a polymerization completely follows chain-end model and catalyst-site control model, respectively.

	(m)	(mm)	(mr)	(rr)	$\frac{4(mm)(rr)}{(mr)^2}$	$\frac{(mr)}{2(rr)}$
Poly(2-PhEtVE)	0.94	0.89	0.08	0.03	19	1.2
Poly(IBVE)	0.90	0.80	0.16	0.04	5.0	2.0
Poly(*n*-PrVE)	0.83	0.69	0.24	0.07	3.4	1.7
Poly(EVE)	0.75	0.51	0.40	0.09	1.2	2.3
Poly(*t*-BuVE)	–	0.49	0.37	0.14	2.0	1.3

Fig. S4 Analysis of triad sequences of isotactic poly(VE)s

References

S1 T. Higashimura, M. Kamigaito, M. Kato, T. Hasebe and M. Sawamoto, *Macromolecules,* 1993, **26**, 2670.

S2 M. Bosch and M. Schlaf, *J. Org. Chem.,* 2003, **68**, 5225.

S3 S. Kigoshi, A. Kanazawa, S. Kanaoka and S. Aoshima, *J. Polym. Sci. Part A: Polym. Chem.* 2019, **57**, 989.

S4 S. Kigoshi, A. Kanazawa, S. Kanaoka and S. Aoshima, *J. Polym. Sci. Part A: Polym. Chem.* 2019, **57**, 2021.

S5 W. A. Lee and G. J. Knight, *Br. Polym. J.*, 1970, **2**, 73.

S6 F. A. Bovey, and G. V. D. Tiers, *J. Polym. Sci.* 1960, **44**, 173.

S7 R. A. Shelden, T. Fueno, T. Tsunetsugu and J. Furukawa, *J. Polym. Sci. Part B: Polym. Lett.,* 1965, **3**, 23.