

Cite this: *Polym. Chem.*, 2024, **15**, 1062

# Dual control of stereoregularity and molecular weight in cationic polymerization of vinyl ether by tunable TADDOLs/TiCl<sub>4</sub> initiating systems†

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The effects of aryl substituents on  $\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) ligands were investigated to develop a TADDOL/TiCl<sub>4</sub> system that simultaneously controls the stereoregularity and molecular weight of poly(isobutyl vinyl ether). Substituents were appropriately designed to generate polymers with relatively high *m* values (80–90%) and narrow molecular weight distributions ( $M_w/M_n = 1.1$ – $1.4$ ) at 0 °C and –78 °C. The steric and electronic effects of TADDOL substituents on the stereoregularity and molecular weight were investigated. Interestingly, conventional fast equilibrium between the dormant C–Cl bonds and active species was likely absent at –78 °C, while the polymerization was mediated by long-lived species, resulting in a linear increase in molecular weights with monomer consumption. This study provides significant insight for the development of high-performance polymerization catalysts through which multiple polymer structures can be simultaneously controlled.

Received 8th December 2023,  
Accepted 5th February 2024

DOI: 10.1039/d3py01353g

rsc.li/polymers

## Introduction

Over the past few decades, numerous efforts have been dedicated to precisely controlling properties of polymer structures, such as their molecular weight (MW), stereoregularity, monomer sequence, and topology, because these properties are closely linked with the properties and functions of polymers.<sup>1</sup> MW and stereoregularity are essential elements of polymer structures but are difficult to simultaneously control. Living polymerization<sup>2–4</sup> and stereospecific polymerization<sup>5–8</sup> are difficult to achieve in natural cationic polymerization of vinyl monomers because the propagating species are highly reactive planar sp<sup>2</sup> carbocations. Nevertheless, progress in polymerization methodologies has enabled various systems to perform living cationic polymerization by suppressing side reactions with appropriate initiators, catalysts, and additives.<sup>9–18</sup> A crucial step in controlling MW is to promote a fast equilibrium between the active and dormant species, through which all propagating chains can evenly propagate at similar rates. Performing stereospecific cationic polymerization is more difficult, although several research groups have created novel stereospecific cationic polymerization systems.<sup>19–37</sup>

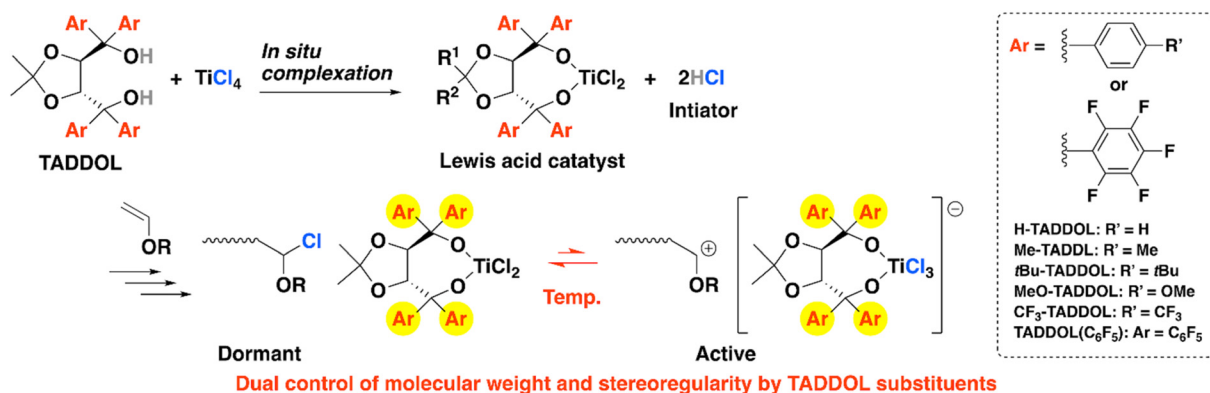
Examples of systems that can simultaneously control stereoregularity and MW in cationic polymerization of vinyl monomers are limited. A few examples have been achieved by combining stereospecific cationic polymerization and degenerative chain-transfer (DT) mechanisms, such as the reversible addition-fragmentation chain transfer (RAFT) mechanism.<sup>28,31,34</sup> In these cases, the counteranions that formed from special initiators and the chain transfer agents separately control the stereoregularity and MW, respectively. On the other hand, a novel high-performance catalyst could control the stereoregularity by forming a special counteranion and control the MW by an atom-transfer mechanism. These catalysts could contribute to the development of polymer chemistry but have been rarely reported in cationic polymerization.<sup>22,23,33</sup>

Previously, we reported the stereospecific cationic polymerization of vinyl ethers (VEs) by using a new initiating system that combined TiCl<sub>4</sub> and a tartaric acid-derived ligand,  $\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL).<sup>26</sup> Through this initiating system, stereospecific polymerization of VEs (*m* = 83–94%) was achieved, but MW control of the resultant polymers was not achieved. We also reported stereospecific living cationic polymerization of *N*-vinylcarbazole by designing zinc-based polymerization catalysts.<sup>23,33</sup> These results motivated us to further develop the TADDOL/TiCl<sub>4</sub> initiating system to simultaneously control the stereoregularity and MW of poly(VE)s. The excellent tunability of TADDOL substituents<sup>38,39</sup> will greatly help researchers design initiating systems.

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† Electronic supplementary information (ESI) available: Experimental section, NMR spectra, and polymerization data. See DOI: <https://doi.org/10.1039/d3py01353g>





**Scheme 1** Cationic polymerization of a VE using the TADDOLs/TiCl<sub>4</sub> initiating system: dual control of MW and stereoregularity by examining TADDOL substituents at various temperatures [(*R,R*)-TADDOL is shown here as an example].

Here, by investigating the effect of TADDOL substituents and reaction conditions, we simultaneously controlled the stereoregularity and MW of poly(VE) with TADDOL/TiCl<sub>4</sub> systems. In this system, the initiator and catalyst are generated by mixing the TADDOL ligands and TiCl<sub>4</sub> (Scheme 1).<sup>40</sup> We show that the TADDOL substituents and the polymerization temperature are the key factors that control the stereoregularity and MW. We also examine the relationship between the electronic/steric effect of TADDOL substituents and the MW/stereoregularity of the resultant polymers.

## Experimental section

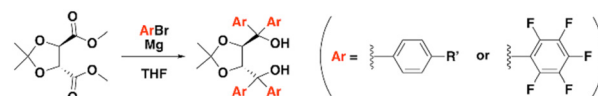
See the ESI<sup>†</sup> for the procedure for TADDOLs synthesis and characterization.

### Materials

Isobutyl vinyl ether (IBVE) (TCI; >99.0%) and ethyl vinyl ether (EVE) (TCI; >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. (4*S*,5*S*)-(–)-2,2-Dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenyl-1,3-dioxolane-4,5-dimethanol (H-TADDOL) (TCI; >97.0%) was used without further purification. Ethyl acetate (Wako; >99.5%) was distilled twice over calcium hydride. Commercially obtained TiCl<sub>4</sub> (Aldrich; 1.0 M solution in toluene) was used without further purification. 1-(Isobutoxy)ethyl chloride [IBVE-HCl; CH<sub>3</sub>CH(O*i*Bu)Cl] was prepared *via* an addition reaction of IBVE with dry HCl, according to a reported method.<sup>41</sup> Hexane (Wako; 96.0%), toluene (Wako; 99.5%), and dichloromethane (Wako; 99.0%) were dried by passage through solvent purification columns (glass contour).

### Procedure for TADDOLs synthesis

TADDOLs were synthesized *via* the Grignard reaction according to the reported method (Scheme 2).<sup>42,43</sup> The typical procedure is described in the ESI.<sup>†</sup>



**Scheme 2** Synthesis of TADDOLs.

### Polymerization procedure

The typical polymerization procedure is as follows. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki, PJ-206A; blow temperature ~450 °C) under dry nitrogen. Hexane and IBVE were sequentially added to the tube using dry syringes. In another tube, a TADDOL solution was added to a solution of TiCl<sub>4</sub> in toluene, and the mixture was left at –78 °C for at least 30 min. The polymerization was initiated by adding the Ti-TADDOLate solution to the monomer solution at –78 °C. After a predetermined time, the reaction was terminated by adding a methanol solution that contained 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-20MUniPort B; GL Sciences Inc.) using hexane as an internal standard.

## Results and discussion

### Effects of polymerization temperature on polymerization using the HT-ADDOL/TiCl<sub>4</sub> initiating system

In cationic polymerization, the MWs of polymers are typically controlled *via* a fast equilibrium between dormant and active species. We assumed that the interconversion between the dormant and active species in the TADDOL/TiCl<sub>4</sub> initiating system would change depending on the polymerization temperature. Therefore, the cationic polymerization of IBVE was conducted with the H-TADDOL/TiCl<sub>4</sub> initiating system (Scheme 1) in hexane/toluene (9/1 v/v) at various temperatures



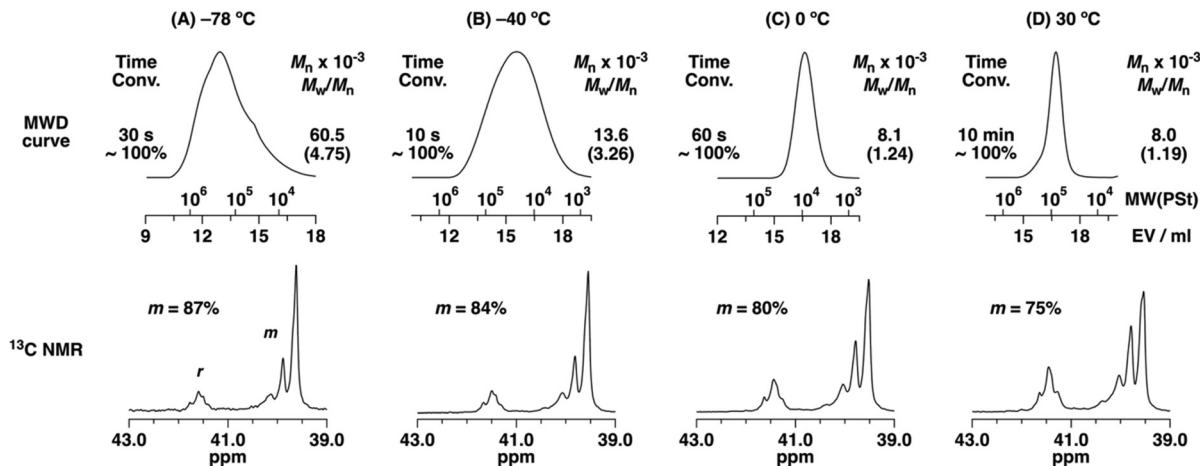


Fig. 1 MWD curves and  $^{13}\text{C}$  NMR spectra of the poly(IBVE)s obtained by the H-TADDOL/ $\text{TiCl}_4$  initiating system at (A)  $-78\text{ }^\circ\text{C}$ , (B)  $-40\text{ }^\circ\text{C}$ , (C)  $0\text{ }^\circ\text{C}$ , and (D)  $30\text{ }^\circ\text{C}$  ( $[\text{IBVE}]_0 = 0.76\text{ M}$ ,  $[\text{H-TADDOL}]_0 = 5.5\text{ mM}$ ,  $[\text{TiCl}_4]_0 = 5.0\text{ mM}$ , in hexane/toluene (9/1 v/v)).

( $-78$  to  $30\text{ }^\circ\text{C}$ ). Fig. 1 (upper) shows the MWD curves of the obtained polymers. A polymer generated at  $-78\text{ }^\circ\text{C}$  exhibited a high MW and broad molecular weight distribution (MWD) ( $M_n = 60.5 \times 10^3$ ,  $M_w/M_n = 4.75$ ), as we reported previously.<sup>26</sup> When the polymerization was conducted at  $-40\text{ }^\circ\text{C}$ , the number-average molecular weight ( $M_n$ ) approached the theoretical value ( $7.7 \times 10^3$ ), while the MWD remained broad ( $M_n = 13.6 \times 10^3$ ,  $M_w/M_n = 3.26$ ). Notably, the polymers obtained at  $0\text{ }^\circ\text{C}$  possessed MWs close to the theoretical value and narrow MWDs ( $M_n = 8.1 \times 10^3$ ,  $M_w/M_n = 1.24$ ; Fig. 1C). The MWs of the polymers increased with increasing monomer conversion (Fig. 2). Structures resulting from side reactions were not observed by  $^1\text{H}$  NMR even for the polymers obtained at quantitative conversion (Fig. S1†). MW control was achieved with the TADDOL/ $\text{TiCl}_4$  system even at  $30\text{ }^\circ\text{C}$  ( $M_n = 8.0 \times 10^3$ ,  $M_w/M_n = 1.19$ ; Fig. 1D).

The isotacticity of the generated polymers increased with decreasing temperature {up to  $m = 87\%$  at  $-78\text{ }^\circ\text{C}$ , Fig. 1 (bottom) and Fig. S2†}. The polymer obtained at  $0\text{ }^\circ\text{C}$  had a

relatively high  $m$  ratio of 80%, demonstrating that MW and stereoregularity were simultaneously controlled. From these results, we found that the polymerization temperature greatly impacted the ability to control MW and stereoregularity. Therefore, we further investigated the cationic polymerization at different temperatures, namely, at  $0\text{ }^\circ\text{C}$  and  $-78\text{ }^\circ\text{C}$ , by using various TADDOLs.

#### Investigation of TADDOL substituents in cationic polymerization of IBVE at $0\text{ }^\circ\text{C}$

Cationic polymerization of IBVE was conducted at  $0\text{ }^\circ\text{C}$  using TADDOLs with various substituents. TADDOLs with different Ar groups {Ar =  $4\text{-R}'\text{C}_6\text{H}_4$  ( $\text{R}' = \text{Me}$ ,  $t\text{Bu}$ ,  $\text{OMe}$ ,  $\text{CF}_3$ ) or  $\text{C}_6\text{F}_5$ , Scheme 1} were synthesized *via* Grignard reactions between a tartaric acid-derived ester and the corresponding aryl bromides (Scheme 2).<sup>42,43</sup> The substituents of TADDOL greatly affected the polymerization behavior (Table 1). In particular, the  $M_n$  values of the poly(IBVE)s obtained at the early stage of the polymerization with Me-TADDOL were closer to the theoretical values (Fig. 3A) than those with H-TADDOL (Fig. 2A). In addition, the poly(IBVE)s obtained with Me-TADDOL exhibited obviously narrower MWDs ( $M_w/M_n \sim 1.10$ ) than those obtained with H-TADDOL. These characteristics indicate that efficient, fast initiation reactions occurred when Me-TADDOL was used. Side reactions were not observed by  $^1\text{H}$  NMR (Fig. 4). Furthermore, the living nature of the polymerization with Me-TADDOL was confirmed by a monomer-addition experiment (Fig. 3B). On the other hand, the MWs of polymers obtained with  $t\text{Bu}$ -,  $\text{MeO}$ -, and  $\text{CF}_3$ -TADDOLs were uncontrollable and the MWDs of the polymers were broad. Notably, the stereoregularity of polymers obtained with Me- and H-TADDOL ( $m = 79\%$  and  $81\%$ , respectively) was higher than that with other TADDOLs. These results showed the potential of the TADDOL/ $\text{TiCl}_4$  initiating system for stereospecific living cationic polymerization. The steric and electronic effects of the TADDOL substituent on the stereoregularity and MW are discussed below.

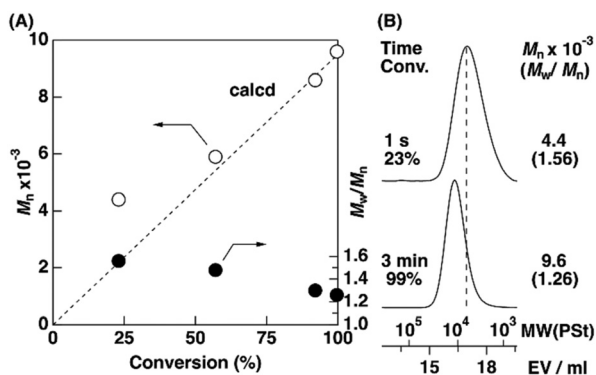


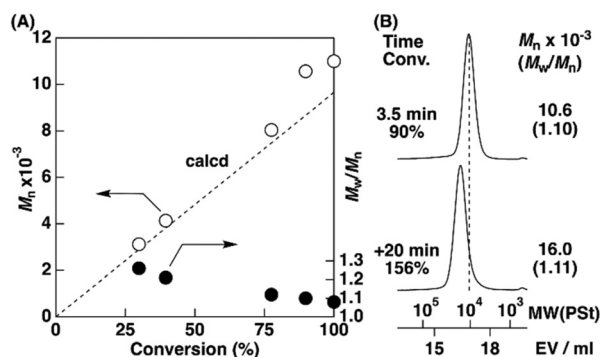
Fig. 2 (A)  $M_n$  and  $M_w/M_n$  values and (B) MWD curves of the poly(IBVE)s obtained by the H-TADDOL/ $\text{TiCl}_4$  initiating system ( $[\text{IBVE}]_0 = 0.76\text{ M}$ ,  $[\text{H-TADDOL}]_0 = 4.4\text{ mM}$ ,  $[\text{TiCl}_4]_0 = 4.0\text{ mM}$ , in hexane/toluene (9/1 v/v) at  $0\text{ }^\circ\text{C}$ ).



**Table 1** Cationic polymerization of IBVE with various TADDOLs (Ar = 4-R'C<sub>6</sub>H<sub>4</sub> (R' = H, Me, tBu, MeO, CF<sub>3</sub>)) at 0 °C<sup>a</sup>

Entry	Ar	Time	Conv. (%)	$M_n \times 10^{-3}$ (calcd) <sup>b</sup>	$M_n \times 10^{-3}$ (obs) <sup>c</sup>	$M_w/M_n$ <sup>c</sup>	<i>m</i> (%)
1	C <sub>6</sub> H <sub>5</sub>	3 min	99	9.5	9.6	1.26	81
2	4-MeC <sub>6</sub> H <sub>4</sub>	8 min	~100	9.6	11.0	1.08	79
3	4- <i>t</i> BuC <sub>6</sub> H <sub>4</sub>	2 h	10	0.1	18.6	7.90	61
4	4-MeOC <sub>6</sub> H <sub>4</sub>	2 h	95	7.3	9.9	23.5	67
5	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2 s	~100	9.6	13.6	3.11	74

<sup>a</sup>[VE]<sub>0</sub> = 0.76 M, [TADDOL]<sub>0</sub> = 4.4 mM (for entry 1), 4.0 mM (for entries 2, 3, and 5), or 5.0 mM (for entry 4), [TiCl<sub>4</sub>]<sub>0</sub> = 4.0 mM (for entries 1–3 and 5) or 5.0 mM (for entry 4). <sup>b</sup>Based on the two protons per TADDOL/TiCl<sub>4</sub> complex. <sup>c</sup>Calculated with polystyrene standards.



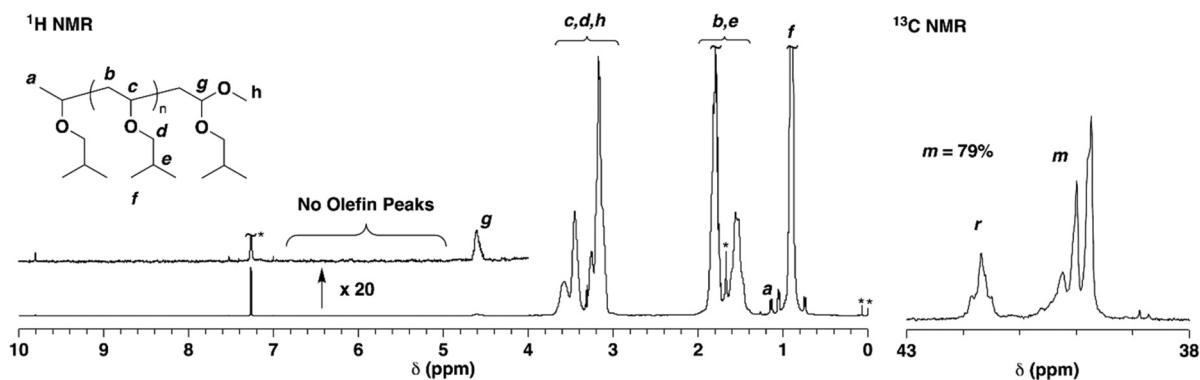
**Fig. 3** (A)  $M_n$  and  $M_w/M_n$  values of the poly(IBVE)s obtained by the Me-TADDOL/TiCl<sub>4</sub> initiating system and (B) MWD curves of the poly(IBVE)s obtained in the monomer-addition experiment ([IBVE]<sub>0</sub> = 0.76 M, [IBVE]<sub>add</sub> = 0.76 M (added when 3.5 min past), [Me-TADDOL]<sub>0</sub> = 4.0 mM, [TiCl<sub>4</sub>]<sub>0</sub> = 4.0 mM, in hexane/toluene (9/1 v/v) at 0 °C).

### Investigation of the TADDOL substituent in the cationic polymerization of IBVE at –78 °C

We next investigated methodologies to control the stereoregularity and MW using TADDOLs with various substituents at –78 °C to attain higher stereoregularity. The polymerization was conducted at lower monomer concentrations ([VE]<sub>0</sub> = 0.10 or 0.20 M) because the reaction solution remained homogeneous and the stereoregularity of the resultant polymers increased at low monomer concentrations, as described in the

previous paper.<sup>26</sup> Various weakly Lewis basic additives,<sup>15</sup> such as esters and ethers, that are typically effective for the living cationic polymerization of VEs were not effective in controlling MWs in this initiating system (Table S1†). In contrast, the substituents of TADDOL had a great impact even at this temperature, although the tendency was different from that at 0 °C (Table 2 and Fig. 5). H- and Me-TADDOLs generated polymers with high stereoregularity (*m* = 90% and 91%, respectively), whereas the MWDs were broad (entries 1 and 2 in Table 2). *t*Bu- and MeO-TADDOLs generated polymers with broad MWDs and lower *m* values (entries 3 and 4 in Table 2). TADDOL with electron-withdrawing C<sub>6</sub>F<sub>5</sub> groups formed a polymer with an MW closer to the theoretical value with a relatively narrow MWD, while the stereoregularity was low (entry 5 in Table 2).

Notably, CF<sub>3</sub>-TADDOL generated polymers with relatively narrow MWDs and high stereoregularity at –78 °C (*m* = 83–84%; entries 6 and 7 in Table 2). Interestingly, adding a small amount of ethyl acetate (entry 8), which functions as a weak Lewis base and potentially interacts with the Ti complex, slowed the reaction and increased the isotacticity (*m* = 90%, Fig. 6C) although excess ethyl acetate (twice the amounts of Ti) decreased the *m* value (entry 3 in Table S2†). Moreover, the MWs of the resultant polymers increased with increasing monomer conversion while maintaining relatively narrow MWDs ( $M_w/M_n$  = 1.2–1.4; Fig. 6A and B), which indicates that long-lived propagating species formed. Although the initiation efficiency was low, this result demonstrates that MW control



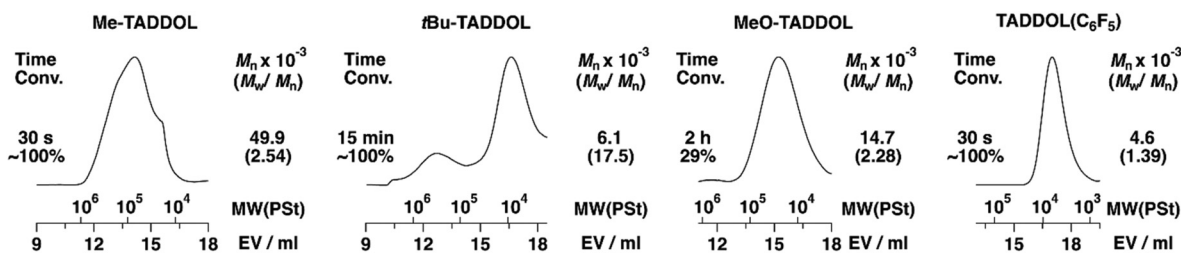
**Fig. 4** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the poly(IBVE) obtained by the Me-TADDOL/TiCl<sub>4</sub> initiating system at 0 °C ([IBVE]<sub>0</sub> = 0.76 M, [Me-TADDOL]<sub>0</sub> = 4.0 mM, [TiCl<sub>4</sub>]<sub>0</sub> = 4.0 mM, in hexane/toluene (9/1 v/v)). \*Water, grease, and TMS.



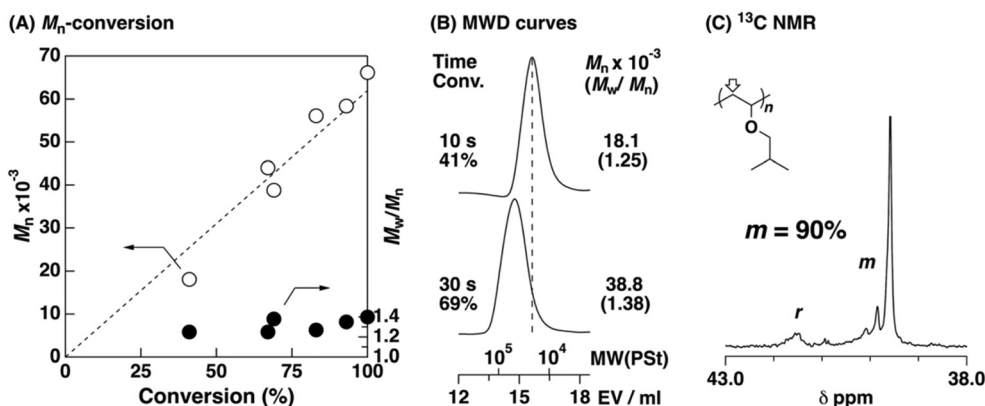
**Table 2** Cationic polymerization of IBVE with various TADDOLs (Ar = 4-R'C<sub>6</sub>H<sub>4</sub> (R' = H, CF<sub>3</sub>, Me, tBu, MeO) or C<sub>6</sub>F<sub>5</sub>) at -78 °C<sup>a</sup>

Entry	Ar	Solvent (v/v)	Time	Conv. (%)	$M_n \times 10^{-3}$ (calcd) <sup>b</sup>	$M_n \times 10^{-3}$ (obs) <sup>c</sup>	$M_w/M_n$ <sup>c</sup>	<i>m</i> (%)
1	C <sub>6</sub> H <sub>5</sub>	Hexane/toluene (9/1)	1 min	~100	1.0	84.9	2.63	90
2	4-MeC <sub>6</sub> H <sub>4</sub>	Hexane/toluene (9/1)	1 min	~100	1.0	49.9	2.54	91
3	4- <i>t</i> BuC <sub>6</sub> H <sub>4</sub>	Hexane/toluene (9/1)	15 min	~100	1.0	6.1	17.5	79
4	4-MeOC <sub>6</sub> H <sub>4</sub>	Hexane/toluene (9/1)	2 h	29	0.3	14.7	2.28	81
5	C <sub>6</sub> F <sub>5</sub>	Toluene	30 s	~100	1.0	4.6	1.39	71
6	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Hexane/toluene (9/1)	30 s	~100	1.0	7.3	1.81	83
7		Toluene	30 s	~100	1.0	7.7	1.45	84
8 <sup>d</sup>		Hexane/toluene (9/1)	30 min	~100	1.0	66.2	1.40	90

<sup>a</sup> [IBVE]<sub>0</sub> = 0.10 M, [TADDOL]<sub>0</sub> = 5.5 mM, [TiCl<sub>4</sub>]<sub>0</sub> = 5.0 mM. <sup>b</sup> Based on the amount of TADDOL/TiCl<sub>4</sub> complex. <sup>c</sup> Calculated with polystyrene standards. <sup>d</sup> Ethyl acetate (5.0 mM) was added.



**Fig. 5** MWD curves of the poly(IBVE)s obtained using various TADDOLs ([IBVE]<sub>0</sub> = 0.10 M, [TADDOL]<sub>0</sub> = 5.5 mM, [TiCl<sub>4</sub>]<sub>0</sub> = 5.0 mM, in toluene or hexane/toluene (9/1 v/v) at -78 °C). The data correspond to entries 2, 3, 4, and 5 in Table 2.



**Fig. 6** (A)  $M_n$  and  $M_w/M_n$  values, (B) MWD curves, and (C) <sup>13</sup>C NMR spectrum of the poly(IBVE)s obtained by the CF<sub>3</sub>-TADDOL/TiCl<sub>4</sub>/ethyl acetate initiating system at -78 °C ([IBVE]<sub>0</sub> = 0.10 M, [CF<sub>3</sub>-TADDOL]<sub>0</sub> = 5.5 mM, [TiCl<sub>4</sub>]<sub>0</sub> = 5.0 mM, [ethyl acetate]<sub>0</sub> = 5.0 mM in hexane/toluene (9/1 v/v)). The data correspond to entry 8 in Table 2.

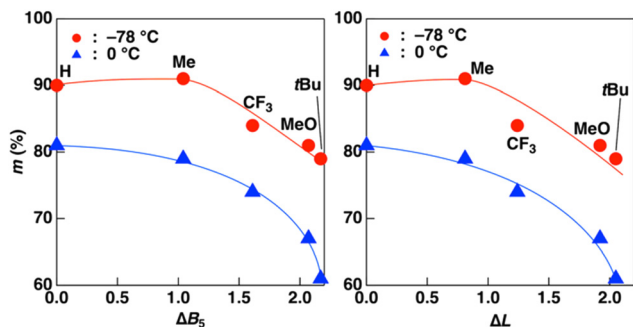
and high stereoregularity were simultaneously achieved by designing the TADDOL substituent. We also confirmed a polymer with a higher molecular weight (conv. ~100%,  $M_n$  = 466 000,  $M_w/M_n$  = 1.67) was obtained at a higher IBVE concentration ([IBVE]<sub>0</sub> = 0.76 M) (entry 4 in Table S2†) although the reaction mixture became heterogeneous because of the polymer precipitation.

### Steric and electronic effects of TADDOL substituents on the control of stereoregularity and MW

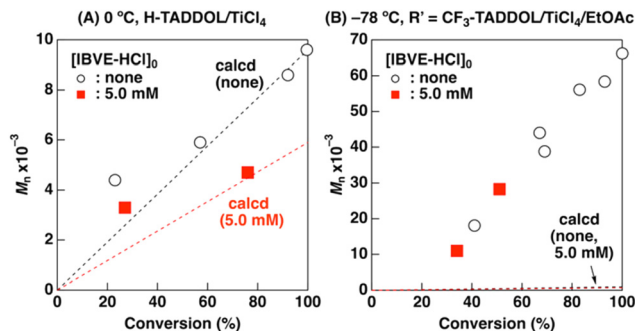
**Effect of TADDOL substituents on stereoregularity.** We examined the effect of TADDOL substituents on the stereospecificity

of the polymerization. The difference between CF<sub>3</sub>-, MeO- and Me-TADDOLs indicates that the electron-withdrawing and electron-donating effects were not striking in terms of stereoregulation at 0 °C (entries 2, 4, and 5 in Table 1) or -78 °C (entries 2, 4, and 6 in Table 2). In contrast, the steric bulkiness of the TADDOL substituents (R' in Scheme 1) had a significant impact. Fig. 7 shows a plot of the stereoregularity of the resultant poly(IBVE)s *versus* the steric bulkiness of the R' group. The steric bulkiness was evaluated with the Sterimol parameters  $B_5$  and  $L$ , which are used to study the quantitative structure-activity relationship (QSAR).<sup>44,45</sup>  $B_5$  and  $L$  represent the maximum width and the length of a substituent, respect-





**Fig. 7** Effects of the bulkiness of the Ar groups in TADDOL on the tacticity of the resultant poly(IBVE)s (Sterimol parameters  $B_5$  and  $L$  represent the maximum width and the length of a substituent, respectively; H, Me,  $CF_3$ , MeO, and  $tBu$  from left to right) ( $[IBVE]_0 = 0.10$  M,  $[TADDOL]_0 = 5.5$  mM,  $[TiCl_4]_0 = 5.0$  mM in hexane/toluene (9/1 v/v)).



**Fig. 8**  $M_n$  values of the poly(IBVE)s obtained in the absence (circles) or the presence (squares) of IBVE-HCl ((A):  $[IBVE]_0 = 0.76$  M,  $[H-TADDOL]_0 = 4.4$  mM,  $[TiCl_4]_0 = 4.0$  mM, in hexane/toluene (9/1 v/v) at 0 °C (B):  $[IBVE]_0 = 0.10$  M,  $[CF_3-TADDOL]_0 = 5.5$  mM,  $[TiCl_4]_0 = 5.0$  mM, [ethyl acetate] $_0 = 5.0$  mM in hexane/toluene (9/1 v/v) at -78 °C).

ively ( $\Delta$  denotes the difference from H). Accordingly, bulky substituents have large  $\Delta B_5$  and  $\Delta L$  values. The stereoregularity of the resultant poly(IBVE)s showed a correlation with  $B_5$  or  $L$  and decreased when  $R'$  had very large  $B_5$  or  $L$  values at 0 °C and -78 °C. This indicates that the bulky  $R'$  group is not suitable for the stereospecific polymerization of IBVE. This trend was also observed in toluene (entries 5–7 in Table S2<sup>†</sup>). In contrast, the stereoregularity of the resultant poly(EVE)s, which have smaller pendants than poly(IBVE), increased when TADDOLs contained bulkier  $R'$  groups, such as  $CF_3$  and  $tBu$  (Table S3 and Fig. S3<sup>†</sup>). For TADDOL( $C_6F_5$ ), which was reported to show a characteristic conformation and strong hydrogen bonds derived from the  $C_6F_5$  groups,<sup>46</sup> we assume that a large change in the conformation of a Ti-TADDOLate complex and the interaction between a Ti-TADDOLate and the propagating cationic species generated the low stereoregularity with this ligand. In addition, 3,5-( $CF_3$ )<sub>2</sub>-TADDOL, which has *m*-disubstituted aryls, was not effective for stereoregulation, either (entries 8 and 9 in Table S2<sup>†</sup>). These results indicate that the stereoregulation of polymers is achieved through an appropriate steric combination of a VE pendant and a Ti-TADDOLate complex.

**Mechanism of MW control.** The change in MW during the polymerization was investigated in more detail. Cationic polymerization of IBVE was conducted using the H-TADDOL/ $TiCl_4$  initiating system with an additional initiator (5.0 mM of IBVE-HCl adduct) at 0 °C (Fig. 8A, red). The MWs of the polymers obtained with IBVE-HCl were lower than those without IBVE-HCl and corresponded well with the theoretical values, which were calculated from the quantities of TADDOL-derived protons and IBVE-HCl at higher conversion. This result suggests that all dormant C-Cl species were activated by the Ti-TADDOLate catalyst. This is the typical behavior of conventional living cationic polymerization *via* the atom-transfer mechanism (Scheme S1A<sup>†</sup>). The effect of TADDOL substituents on the MW in Table 1 likely originated from the change in balance between initiation and propagating rates; Me-TADDOL appropriately slowed the propagating reaction (Fig. S4<sup>†</sup>) by its

slight steric bulkiness and generated polymers with narrow MWDs.

In contrast, the MWs of the obtained polymers were much higher than the theoretical values at any conversion at -78 °C (Fig. 8B), even when IBVE-HCl was used. IBVE-HCl did not affect the MWs of the resultant polymers (Fig. 8B, red), suggesting that dormant C-Cl species were scarcely activated by the catalyst at this temperature and that one Ti-TADDOLate counteranion probably attached to one propagating chain end (Scheme S1B<sup>†</sup>). Very small amounts of propagating carbocations were rapidly generated by the  $CF_3$ -TADDOL/ $TiCl_4$ /ethyl acetate initiating system, and subsequently, the generated carbocations with the bulky Ti-TADDOLate counteranion propagated without undergoing side reactions. These results indicate that MW control may have occurred with “long-lived” propagating cations that do not rely on conventional fast dormant-active equilibrium, and this process occurred in a similar manner to living anionic polymerization.

To reveal the nature of the propagating species, the effect of polymerization conditions was further investigated. Solvents and temperatures exhibited an extraordinary impact on the reaction rate with the TADDOL/ $TiCl_4$  initiating system (Table S4<sup>†</sup>). Surprisingly, the reaction was accelerated with decreasing solvent polarity (dielectric constant) and temperature. This is opposite to the behavior observed in many ionic reactions. The temperature effect suggests that formation of dormant species may be suppressed at low temperatures.<sup>47</sup> In addition, considering that many titanium catalysts form dimers (oligomers),<sup>48–50</sup> lower solvent polarity and lower temperature possibly enhance dimerization or oligomerization of titanium catalysts. These “assembled” catalysts most likely possess higher activity than their monomeric counterparts. Previous studies revealed that the cationic polymerization of isobutene with  $TiCl_4$  accelerates at lower temperatures and is catalyzed by two  $TiCl_4$  per active species.<sup>51–53</sup> The trend is similar to that found in this study, although increasing solvent polarity accelerates the isobutene polymerization reaction. The assembly of the Ti-TADDOLate catalyst may be responsible for



the unique nature of the propagating species shown above at  $-78\text{ }^{\circ}\text{C}$ .

## Conclusion

Simultaneous control of the MWs and stereoregularity of poly(IBVE) was achieved with the TADDOL/TiCl<sub>4</sub> initiating system by utilizing appropriate TADDOL substituents. H- and Me-TADDOL generated polymers with narrow MWDs and a relatively high stereoregularity at  $0\text{ }^{\circ}\text{C}$ . The use of CF<sub>3</sub>-TADDOL led to stereospecific cationic polymerization of IBVE with long-lived propagating species even at  $-78\text{ }^{\circ}\text{C}$ , whereas the nature of the propagating species was different from that at  $0\text{ }^{\circ}\text{C}$ . An appropriate steric combination of VE pendant and Ti-TADDOLate complex was responsible for the stereospecific polymerization. This study provides advances in the precise design of catalysts as in organic chemistry and coordination polymerization, which has been difficult to achieve in cationic polymerization.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was partially supported by JSPS KAKENHI grant numbers 18J20555 and 17H03068.

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