

Supporting Information for:
**Metal-Free Living Cationic Polymerization Using Diaryliodonium Salts as
Organic Lewis Acid Catalysts**

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References

Table S1. Cationic Polymerization of IBVE Using **1** with Various Cationogens^a

Entry	Cationogen	[<i>n</i> Bu ₄ NCl] ₀ (mM)	Time (h)	Conversion (%)	<i>M_n</i> × 10 ⁻³ (calcd)	<i>M_n</i> × 10 ⁻³ (GPC) ^b	<i>M_w</i> / <i>M_n</i> (GPC) ^b
1	TfOH/ <i>n</i> Bu ₄ NCl	0.2 ^c	338	77	8.8	8.9	1.11
2	IBVE-HCl	0	8	92	10.6	6.3	3.89
3	IBVE-HCl	0.2	291	95	11.0	10.4	1.14
4	HCl ^d	0	21	98	11.3	10.3	2.58
5	HCl ^d	0.2	292	92	10.6	11.6	1.11

^a [IBVE]₀ = 0.46 M, [cationogen]₀ = 4.0 mM, [*n*Bu₄NCl]₀ = 0 (entries 2 and 4), 0.2 (entries 3 and 5), or 4.2 (entry 1) mM, [**1**]₀ = 2.0 mM, in dichloromethane at -40 °C. ^b By GPC using polystyrene standards.

^c Concentrations of *n*Bu₄NCl not consumed for the generation of a cationogen via the reaction with TfOH: [*n*Bu₄NCl]_{excess} = [*n*Bu₄NCl]₀ - [TfOH]₀. ^d [Et₂O]₀ = 4.0 mM.

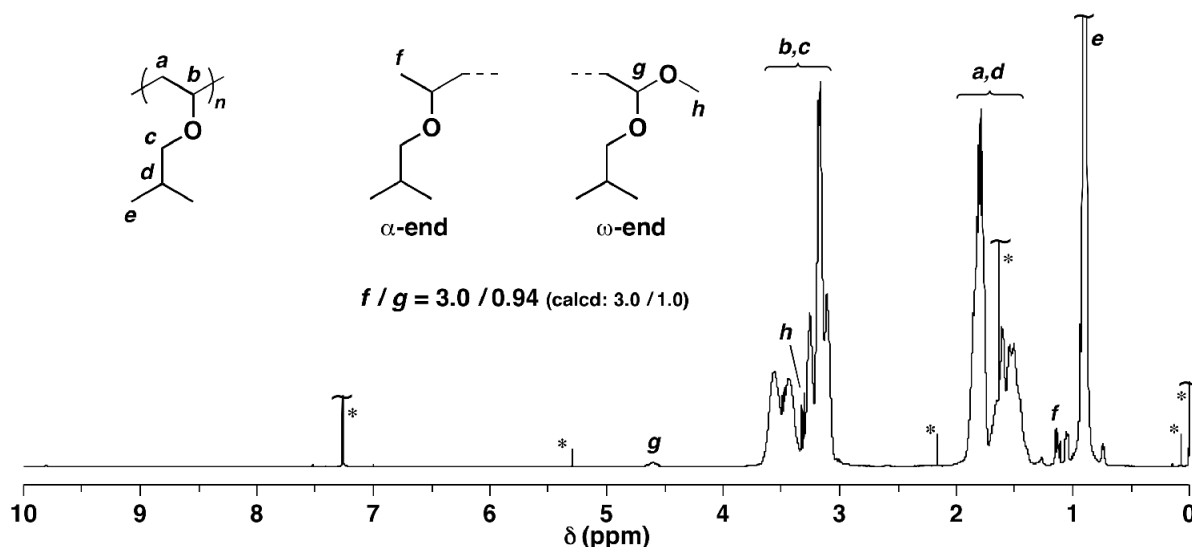


Figure S1. ¹H NMR spectrum (in CDCl₃ at 30 °C) of poly(IBVE) obtained using **1** (the same polymerization conditions to those used for Figure 2; * water, grease, TMS, acetone, dichloromethane, and CHCl₃).

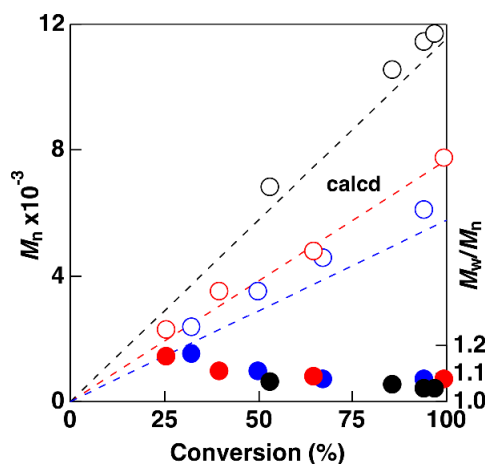


Figure S2. M_n and M_w/M_n values of the products obtained in the polymerization of IBVE at different concentrations of cationogens. Polymerization conditions: $[\text{IBVE}]_0 = 0.46 \text{ M}$, $[\text{TfOH}]_0 = 4.0$ (black), 6.0 (red), or 8.0 (blue) mM, $[\text{nBu}_4\text{NI}]_0 = 4.2$ (black), 6.3 (red), or 8.4 (blue) mM, $[\mathbf{1}]_0 = 2.0 \text{ mM}$ in dichloromethane at -40°C . The data corresponds to those shown in Figure 4.

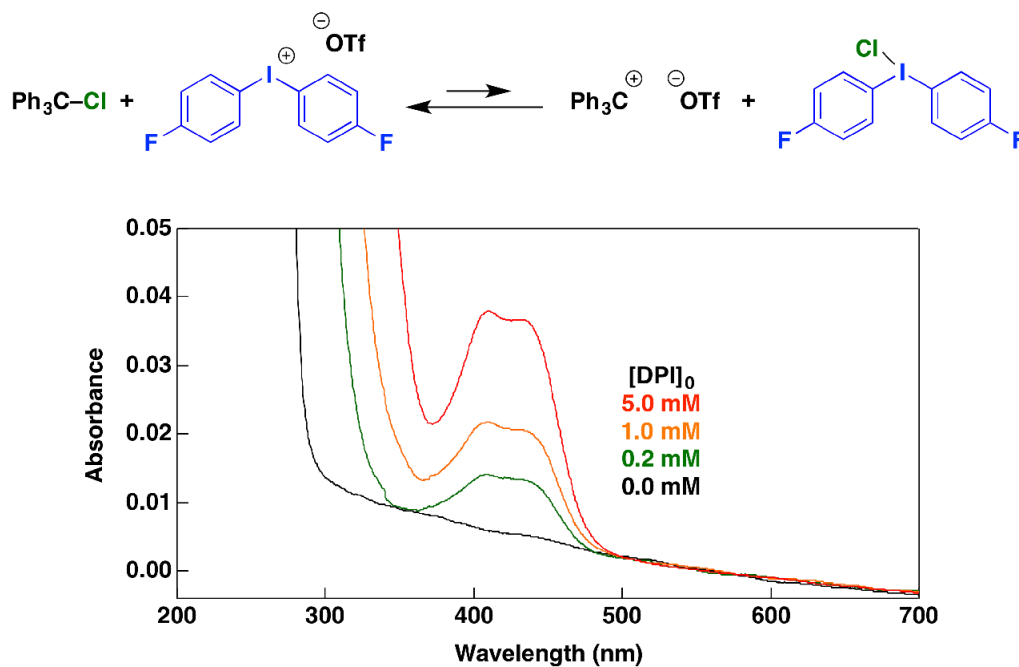


Figure S3. Preliminary experiments for estimating the ionization ability diaryliodonium salts based on the absorbance of the trityl cation^{S1} generated from trityl chloride ($[\mathbf{1}]_0 = 0\text{--}5.0 \text{ mM}$, $[\text{Ph}_3\text{CCl}]_0 = 0.2 \text{ mM}$, in dichloromethane at 15°C).

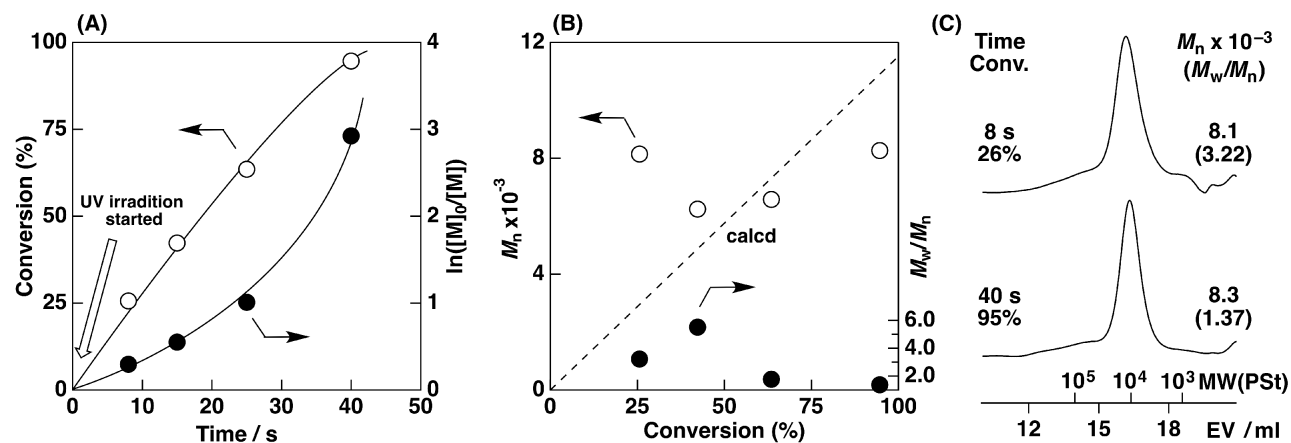


Figure S4. (A) Time–conversion curves and first order plot of the polymerization of IBVE, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. UV light was irradiated soon after the initiation of the polymerization [UV source: 250 W high-pressure mercury lamp (Ushio, SP-9)]. Polymerization conditions: $[IBVE]_0 = 0.46$ M, $[TfOH]_0 = 4.0$ mM, $[nBu_4NI]_0 = 4.2$ mM, $[3]_0 = 2.0$ mM, in dichloromethane at -40 °C.

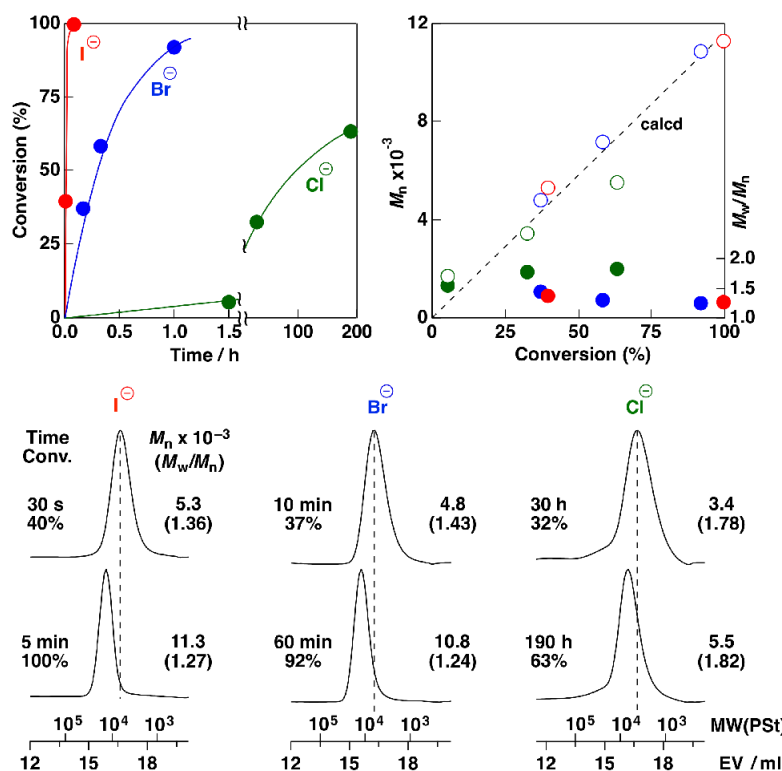


Figure S5. (A) Time–conversion curves of the polymerization of IPVE, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[IPVE]_0 = 0.54$ M, $[TfOH]_0 = 4.0$ mM, $[nBu_4NX]_0 = 4.2$ mM (X = I, Br, or Cl), $[3]_0 = 2.0$ mM in dichloromethane at -40 °C.

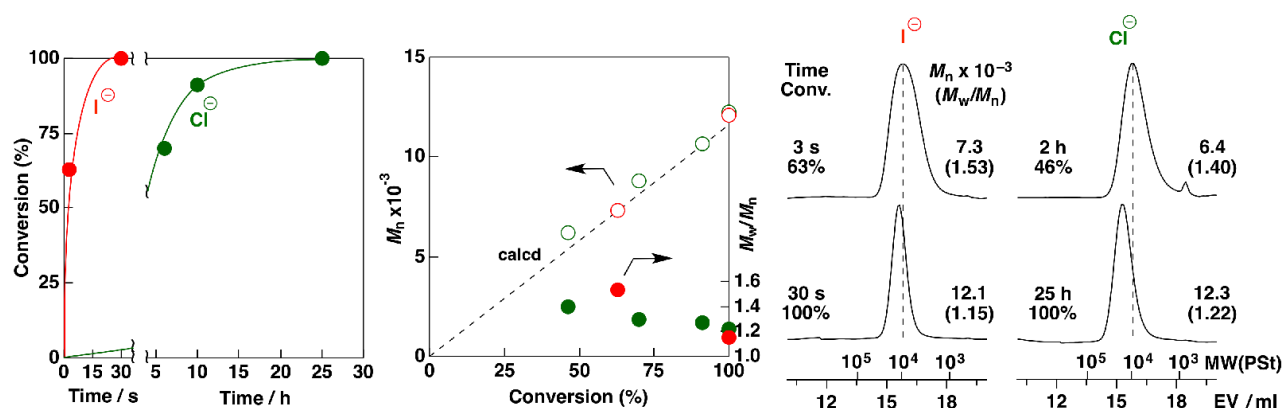


Figure S6. (A) Time–conversion curves of the polymerization of IPVE, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[IPVE]_0 = 0.54$ M, $[TfOH]_0 = 4.0$ mM, $[nBu_4NX]_0 = 4.2$ mM (X = I, or Cl), $[1]_0 = 2.0$ mM in dichloromethane at -40 °C.

Note for Figures S5 and S6: IPVE, which is a more reactive VE than IBVE, was used in Figures S5 and S6 because the polymerization of IBVE with a cationogen with a Cl atom requires very long reaction time (Table S1).

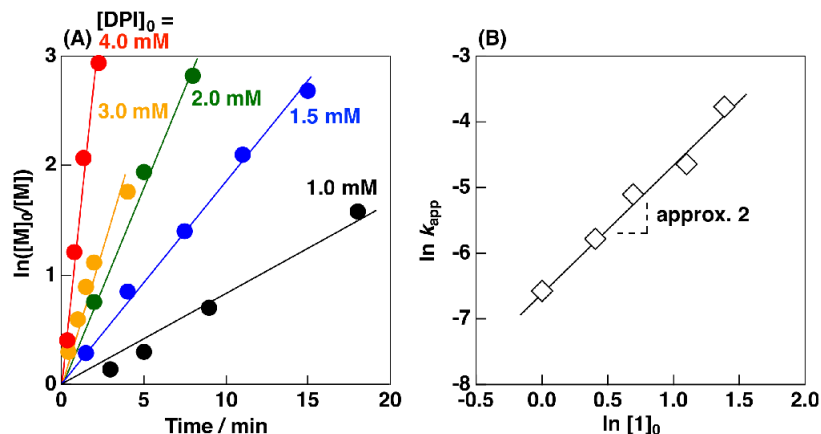


Figure S7. (A) First-order plots of the polymerization of IBVE using **1** and (B) the dependence of k_{app} (s^{-1}) on $[1]_0$. Polymerization conditions: $[IBVE]_0 = 0.46$ M, $[TfOH]_0 = 4.0$ mM, $[nBu_4NI]_0 = 4.2$ mM, $[1]_0 = 1.0$ (black), 1.5 (blue), 2.0 (green; the same data to those shown in Figure 2), 3.0 (orange), and 4.0 (red) mM, in dichloromethane at -40 °C. The time–conversion curves are shown in Figure 5.

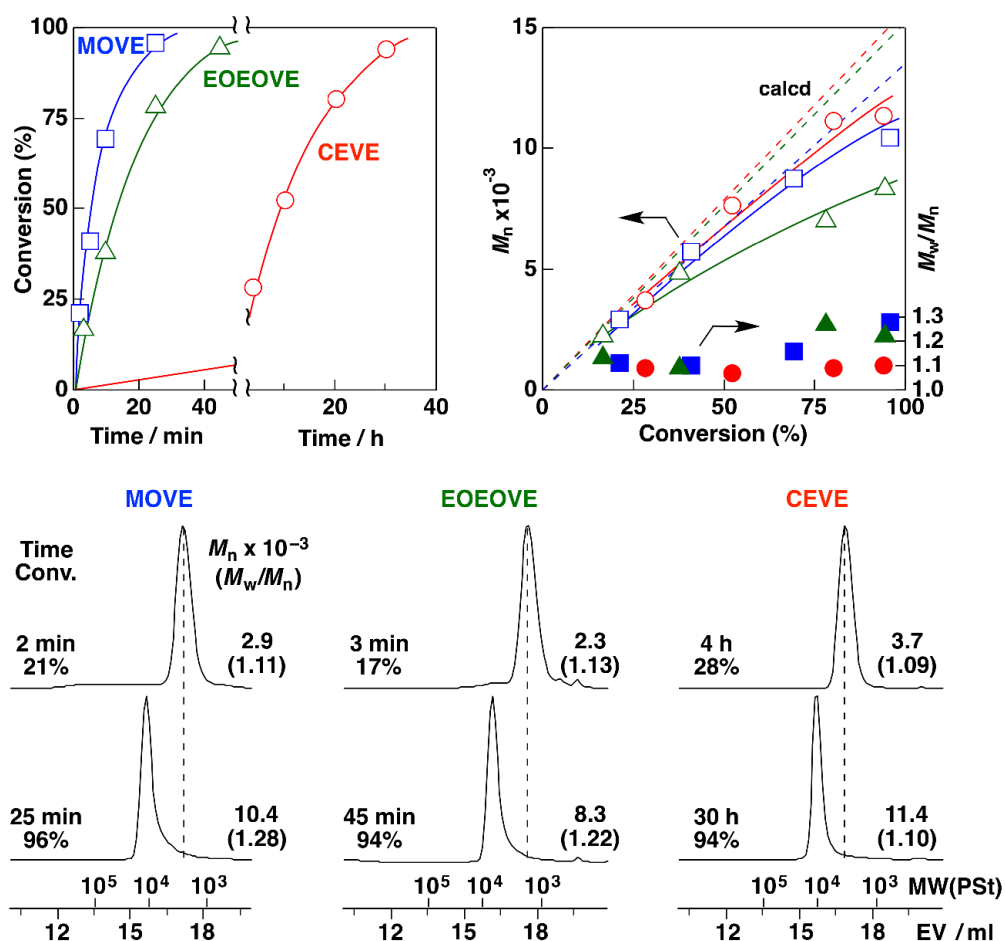


Figure S8. (A) Time–conversion curves of the polymerization of CEVE, MOVE, and EOEOVE; (B) M_n and M_w/M_n values; and (C) MWD curves of the obtained polymers. Polymerization conditions: $[CEVE]_0 = 0.59$ M, $[MOVE]_0 = 0.53$ M, $[EOEOVE]_0 = 0.38$ M, $[TfOH]_0 = 4.0$ mM, $[nBu_4NI]_0 = 4.2$ mM, $[1]_0 = 2.0$ mM in dichloromethane at -40 °C. The data correspond to entries 7–9 in Table 1.

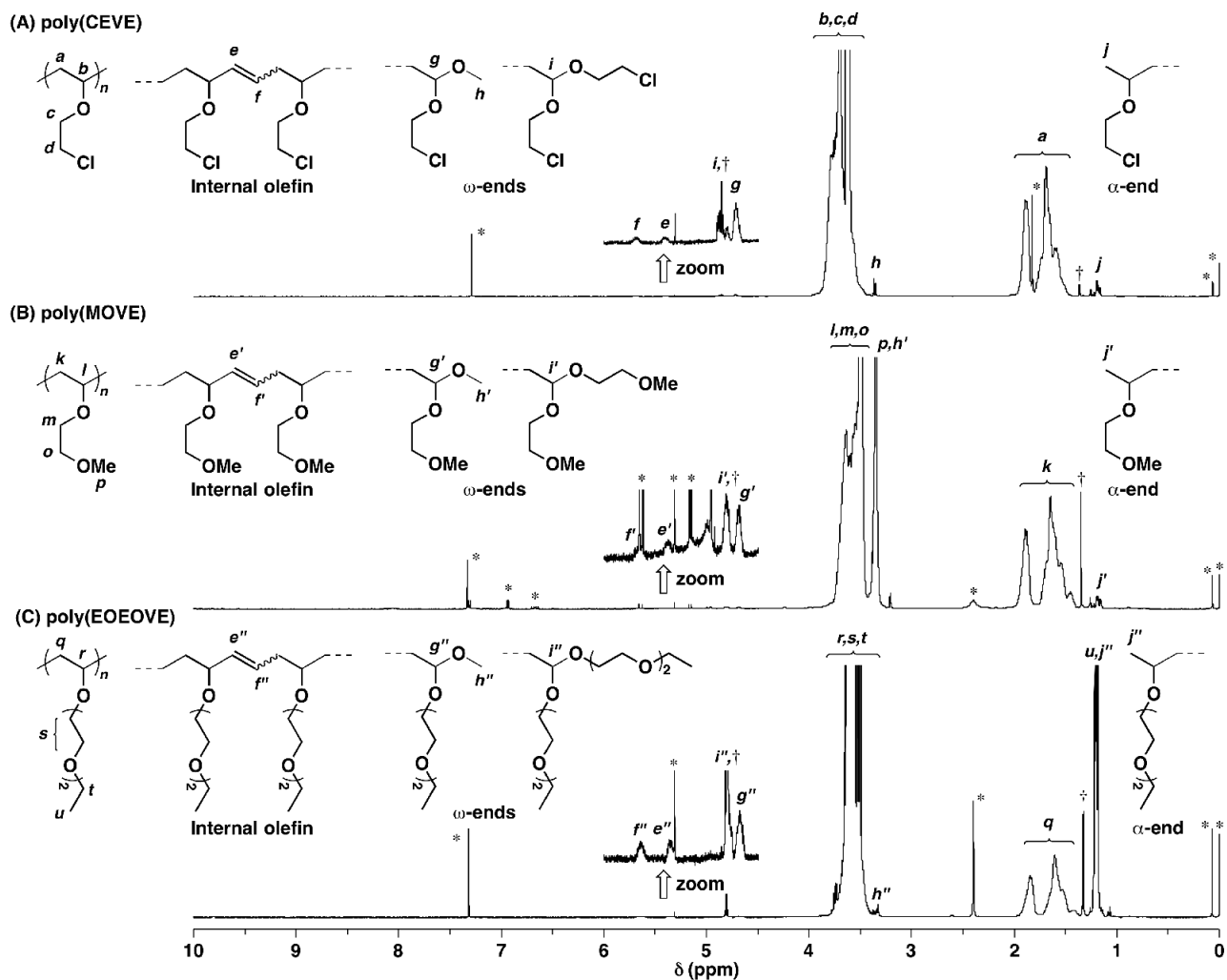
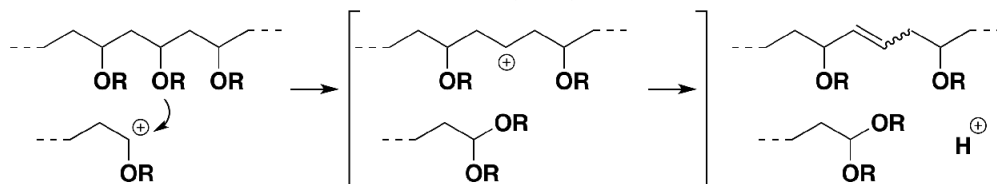


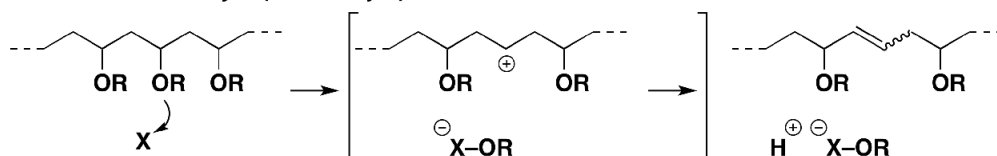
Figure S9. ^1H NMR spectra of (A) poly(CEVE), (B) poly(MOVE), and (C) poly(EOEVE) obtained using **1** as a catalyst. See Figure S8 for the polymerization conditions. The data correspond to the lower MWD curves in Figure S8. Peaks at 1.3 ppm and 4.8 ppm (†) are likely assignable to an acetal generated from a VE and an alcohol derived from the side chain of a VE. * TMS, grease, water, chloroform, dichloromethane, or contaminants.

Note for Figures S8 and S9: The M_n values of the poly(CEVE)s, poly(MOVE)s, and poly(EOEOVE)s deviated from the theoretical line at high monomer conversion (Figure S8). In addition, peaks assignable to internal olefin structures (peaks at 5.3 and 5.6 ppm) were observed in the ^1H NMR spectra of the polymers (Figure S9). These results suggest that chain transfer reactions likely occurred via alcohol elimination. Specifically, an alkoxy group is abstracted from the polymer chain via the intra- or intermolecular reaction with the propagating carbocation and/or the reaction with a catalyst.^{S2,S3} The reactions liberates a proton, which generates a new propagating chain.

(A) Intra- or intermolecular reaction with the propagating carbocation



(B) Reaction with a catalyst ($\text{X} = \text{catalyst}$)



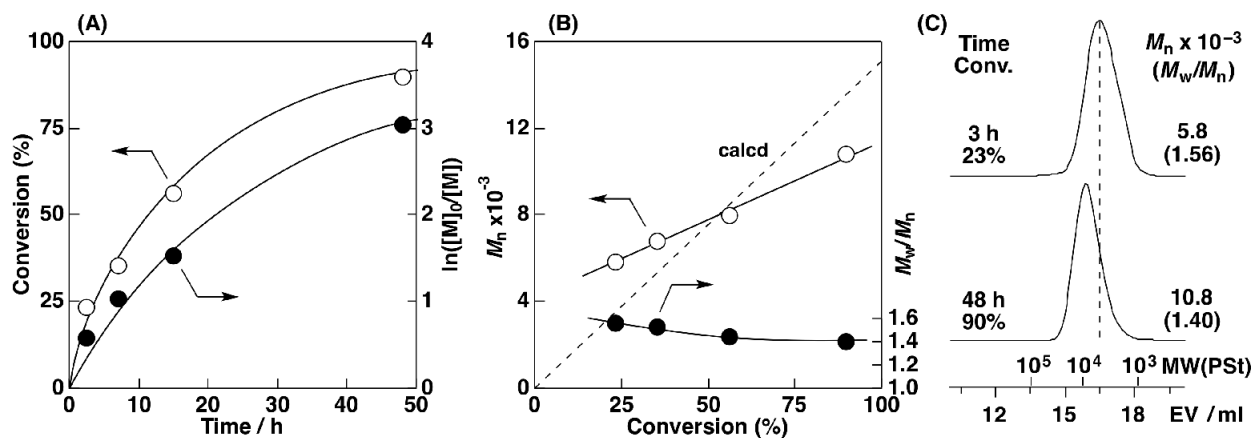


Figure S10. (A) Time–conversion curves of the polymerization of pMOS, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[pMOS]_0 = 0.45$ M, $[TfOH]_0 = 4.0$ mM, $[nBu_4NI]_0 = 4.2$ mM, $[1]_0 = 4.0$ mM in dichloromethane at -40 °C. The data correspond to entry 10 in Table 1.

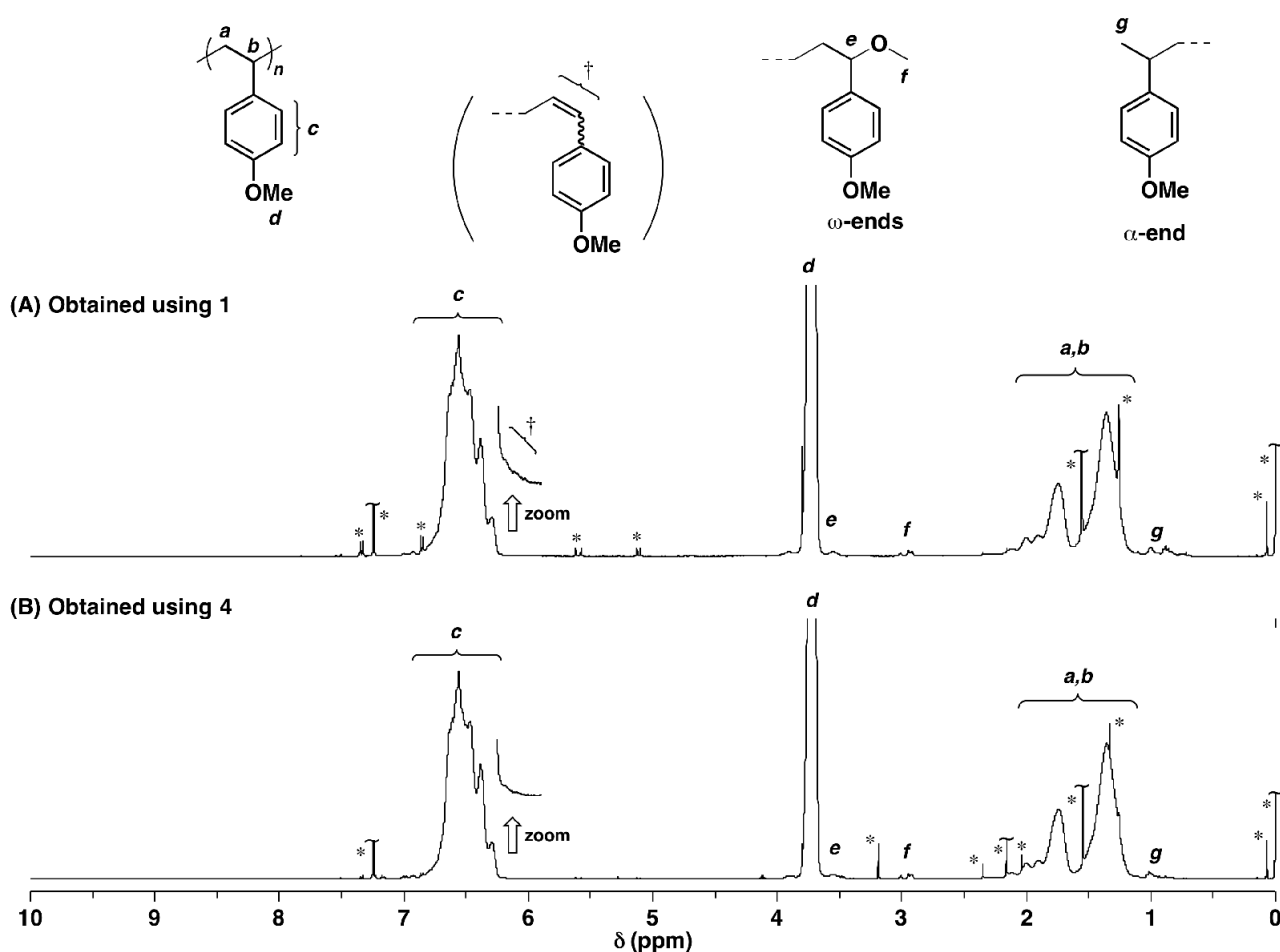


Figure S11. 1H NMR spectra of poly(pMOS)s obtained using (A) **1** (entry 10 in Table 1; Figure S10) or (B) **4** (entry 11 in Table 1; Figure 8). † The structure resulting from β -proton elimination was difficult to detect probably because of the infrequent occurrence. * TMS, grease, water, residual monomer, chloroform, etc.

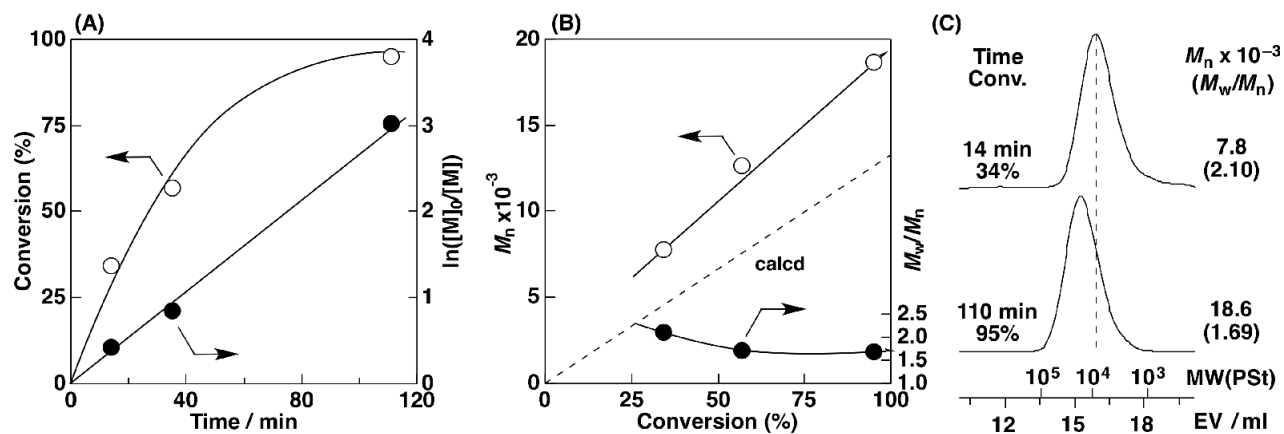


Figure S12. (A) Time–conversion curves of the polymerization of pMeSt, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[pMeSt]_0 = 0.45$ M, $[IBVE-HCl]_0 = 4.0$ mM, $[nBu_4NI]_0 = 0.6$ mM, $[4]_0 = 4.0$ mM, $[1]_0 = 2.0$ mM in dichloromethane at -40 °C. The data correspond to entry 13 in Table 1.

Note for Figure S12: The M_n values of the poly(pMeSt)s were larger than the theoretical values. The result suggests that the initiation efficiency is relatively low although the reason is unclear.

References

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- S3. Shimomoto, H.; Kanaoka, S.; Aoshima, S. Precise Synthesis of End-Functionalized Thermosensitive Poly(vinyl ether)s by Living Cationic Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 4137–4144.