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Electronic Supplementary Information:

Synthesis of Block or Graft Copolymers Containing Poly(Styrene Derivatives) Segments by Living Cationic Polymerization Using Acetal Moieties as Latent Initiating Sites

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Contents:

Figure S1. MWD curves for poly(pMeSt)s obtained using the TME/Lewis acid initiating systems

Figure S2. MWD curve and ¹H NMR spectrum for polystyrene obtained using the TME-TiCl₄/SnCl₄ initiating system

Figure S3. MWD curves for poly(pMeSt)s obtained using the TME-TiCl₄/SnCl₄ initiating system

Figure S4. MWD curves for the synthesis of poly(IBVE)-*block*-poly(pMeSt) through sequential block copolymerization

Figure S5. MWD curves for the synthesis of poly(IBVE-co-DMEVE)-graft-poly(pMeSt) using poly(IBVE-co-DMEVE) as a macroinitiator

Figure S6. ¹H NMR spectrum of poly(IBVE-co-DMEVE)-graft-poly(pMeSt) after hydrolysis

Figure S7. DSC thermograms for poly(IBVE-*co*-DMEVE), poly(pMeSt), poly(IBVE)-*block*-poly(pMeSt) and poly(IBVE-*co*-DMEVE)-*graft*-poly(pMeSt)

Figure S8. ¹H NMR spectra of poly(IBVE-co-DMEVE)-graft-poly(pMOS)

Figure S9. ¹H NMR spectra of poly(IBVE-*co*-DMEVE)-*graft*-poly(tBOS)

Figure S10. MWD curves for the synthesis of poly(IBVE-co-DMEVE)-graft-poly(tBOS) using poly(IBVE-co-DMEVE) as a macroinitiator

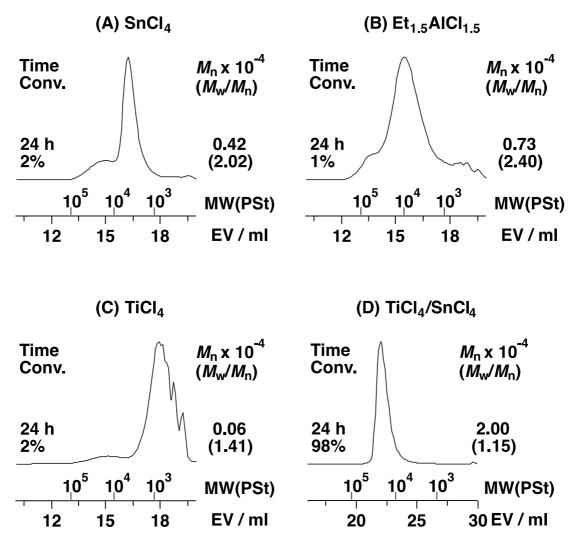
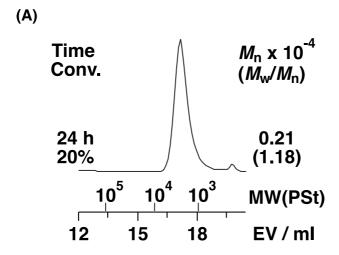


Figure S1. MWD curves for poly(pMeSt)s obtained using the TME/Lewis acid initiating systems: $[pMeSt]_0 = 0.76 \text{ M}$, $[TME]_0 = 4.0 \text{ mM}$, $[Lewis Acid]_0 = 20 \text{ mM}$ (Et_{1.5}AlCl_{1.5} and TiCl₄) or 10 mM (SnCl₄), or 5.0/10 mM (TiCl₄/SnCl₄), $[DTBP]_0 = 10 \text{ mM}$, [ethyl acetate] = 50 mM, in CH₂Cl₂ at 0 °C.



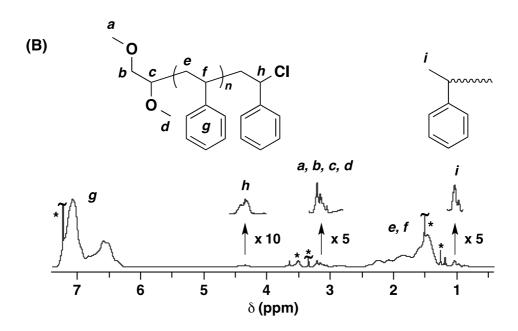


Figure S2. (A) MWD curve of the obtained polystyrene using the TME-TiCl₄/SnCl₄ initiating system: $[St]_0 = 0.87 \text{ M}$, $[TME]_0 = 4.0 \text{ mM}$, $[TiCl_4]_0 = 5.0 \text{ mM}$, $[SnCl_4]_0 = 20 \text{ mM}$, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH_2Cl_2 at 0 °C (B) ¹H NMR spectrum of polystyrene (500.16 MHz, CDCl₃, 30 °C; * solvent, vaseline, water, etc.).

(A) Without Additives (B) Without Proton Trap $M_{\rm n} \times 10^{-4}$ $(M_{\rm w}/M_{\rm n})$ **Time Time** Conv. Conv. 8 h 8 h 0.66 0.91 99% 97% (1.24)(2.05)1,05 10³MW(PSt) MW(PSt) 12 18 EV/ml 15 EV/ml 15 18 12

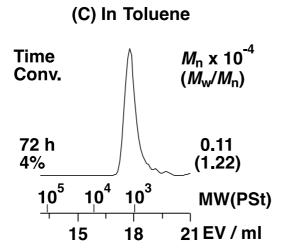
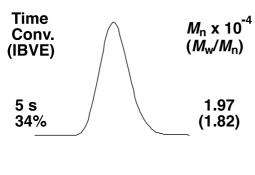


Figure S3. MWD curves for poly(pMeSt)s obtained using the TME-TiCl₄/SnCl₄ initiating system: [pMeSt]₀ = 0.76 M, [TME]₀ = 4.0 mM, [TiCl₄]₀ = 5.0 mM, [SnCl₄]₀ = 10 mM, [DTBP] = 0 (A and B) or 10 mM (C), [ethyl acetate] = 0 (A) or 50 mM (B and C), in CH₂Cl₂ (A and B) or toluene (C) at 0 °C.

(A) Optimized for IBVE (B) Optimized for IBVE + Additional SnCl₄ Time Time $M_{\rm n} \times 10^{-4}$ $(M_{\rm w}/M_{\rm n})$ $M_{\rm n} \times 10^{-4}$ $(M_{\rm w}/M_{\rm n})$ Conv. Conv. (IBVE, pMeSt) (IBVE, pMeSt) 0.64 30 s 30 s 0.57 87%, -88%, -(1.20)(1.23)30 s 30 s +8 h 0.71 +8 h 0.29 100%, ~1% 100%, 7% (1.18)(2.06)MW(PSt) MW(PSt) 12 15 18 EV / ml 12 15 18 EV / ml





n.d.*

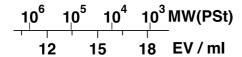


Figure S4. MWD curves for the synthesis of poly(IBVE)-*block*-poly(pMeSt) through sequential block copolymerization: (A) [IBVE] $_0 = 0.46$ M, [IBEA] $_0 = 4.0$ mM, [Et $_{1.5}$ AlCl $_{1.5}$] $_0 = 2.5$ mM, [SnCl $_4$] $_0 = 10$ mM, [pMeSt] $_{add} = 0.51$ M, [ethyl acetate] = 1.0 M, in toluene at 0 °C (B) [IBVE] $_0 = 0.46$ M, [IBEA] $_0 = 4.0$ mM, [EtAlCl $_2$] $_0 = 2.5$ mM, [SnCl $_4$] $_0 = 10$ mM, [pMeSt] $_{add} = 0.51$ M, [SnCl $_4$] $_{add} = 80$ mM, [ethyl acetate] = 1.0 M, in toluene at 0 °C (C) [IBVE] $_0 = 0.76$ M, [IBEA] $_0 = 4.0$ mM, [Et $_{1.5}$ AlCl $_{1.5}$] $_0 = 5.0$ mM, [ethyl acetate] = 50 mM, in CH $_2$ Cl $_2$ at 0 °C. *The subsequent addition of pMeSt was not conducted because the first segment was not synthesized precisely.

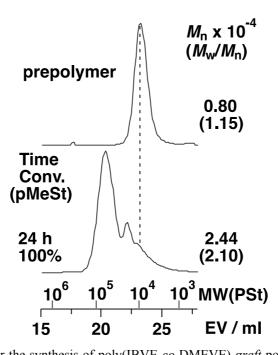


Figure S5. MWD curves for the synthesis of poly(IBVE-co-DMEVE)-graft-poly(pMeSt) using poly(IBVE-co-DMEVE) as a macroinitiator: [pMeSt]₀ = 0.76 M, [acetal units]₀ = 4.0 mM, [TiCl₄]₀ = 10 mM, [SnCl₄]₀ = 10 mM, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH₂Cl₂ at 0 °C.

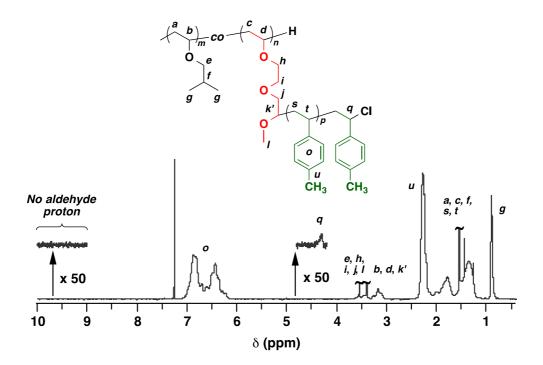


Figure S6. ¹H NMR spectrum of poly(IBVE-co-DMEVE)-graft-poly(pMeSt) [M_n (GPC) = 5.02 × 10⁴, M_w/M_n (GPC) = 1.24] after hydrolysis^a (500.16 MHz, CDCl₃, 30 °C).

^a Hydrolysis conditions: [poly(IBVE-co-DMEVE)-graft-poly(pMeSt)] $_0 = 3.0$ mg/mL, [HCl] $_0 = 0.5$ M in 1,2-dimethoxyethane at room temperature.

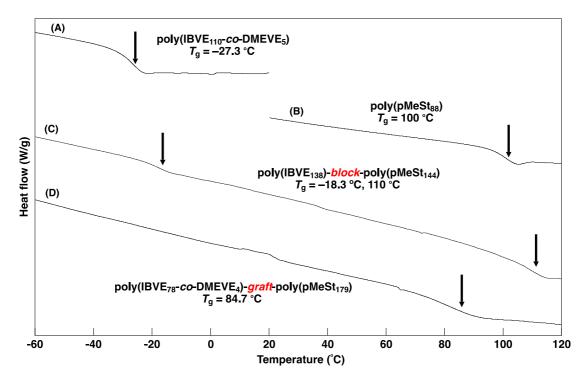
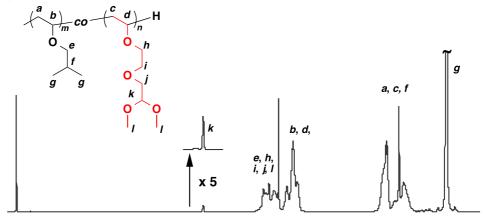


Figure S7. DSC thermograms for (A) poly(IBVE₁₁₀-co-DMEVE₅) ($M_n = 1.19 \times 10^4$, $M_w/M_n = 1.13$), (B) poly(pMeSt₈₈) ($M_n = 1.04 \times 10^4$, $M_w/M_n = 1.19$), (C) poly(IBVE₁₃₈)-block-poly(pMeSt₁₄₄) ($M_n = 3.81 \times 10^4$, $M_w/M_n = 1.12$) and (D) poly(IBVE₇₈-co-DMEVE₄)-graft-poly(pMeSt₁₇₉) ($M_n = 5.69 \times 10^4$, $M_w/M_n = 1.22$).

(A) poly(IBVE-co-DMEVE)



(B) poly(IBVE-co-DMEVE)-garft-poly(pMOS)

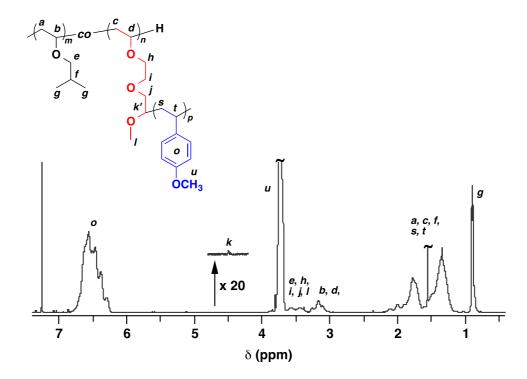
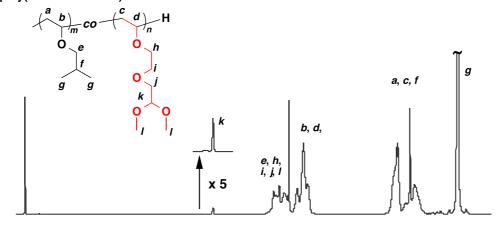


Figure S8. ¹H NMR spectra of poly(IBVE-*co*-DMEVE)-*graft*-poly(pMOS) [M_n (GPC) = 6.70 × 10⁴, M_w/M_n (GPC) = 1.30] (B) and the linear macroinitiator [M_n (GPC) = 0.87 × 10⁴, M_w/M_n (GPC) = 1.12] (A) (500.16 MHz, CDCl₃, 30 °C).

(A) poly(IBVE-co-DMEVE)



(B) poly(IBVE-co-DMEVE)-garft-poly(tBOS)

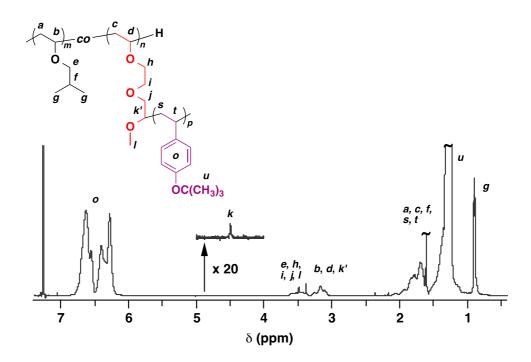


Figure S9. ¹H NMR spectra of poly(IBVE-*co*-DMEVE)-*graft*-poly(tBOS) [M_n (GPC) = 13.9 × 10⁴, M_w/M_n (GPC) = 1.58] (B) and the linear macroinitiator [M_n (GPC) = 1.69 × 10⁴, M_w/M_n (GPC) = 1.10] (A) (500.16 MHz, CDCl₃, 30 °C).

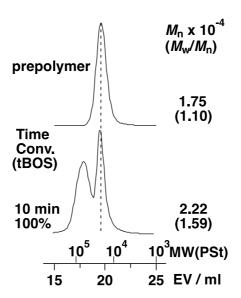


Figure S10. MWD curves for the synthesis of poly(IBVE-co-DMEVE)-graft-poly(tBOS) using poly(IBVE-co-DMEVE) as a macroinitiator: $[tBOS]_0 = 0.53$ M, $[acetal units]_0 = 4.8$ mM, $[TiCl_4]_0 = 10$ mM, $[SnCl_4]_0 = 10$ mM, [DTBP] = 10 mM, [ethyl acetate] = 0.50 M, in CH_2Cl_2 at 0 °C.