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

Norifumi Yokoyama, Hirotoshi Yoshida, Arihiro Kanazawa, Shokyoku Kanaoka, and Sadahito Aoshima*

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

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Figure S1. MWD curves for poly(pMeSt)s obtained using the TME/Lewis acid initiating systems: [pMeSt]₀ = 0.76 M, [TME]₀ = 4.0 mM, [Lewis Acid]₀ = 20 mM (Et₁.₅AlCl₁.₅ and TiCl₄) or 10 mM (SnCl₄), or 5.0/10 mM (TiCl₄/SnCl₄), [DTBP]₀ = 10 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 M, [TME]₀ = 4.0 mM, [TiCl₄]₀ = 5.0 mM, [SnCl₄]₀ = 20 mM, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH₂Cl₂ at 0 °C (B) ¹H NMR spectrum of polystyrene (500.16 MHz, CDCl₃, 30 °C; * solvent, vaseline, water, etc.).
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 ºC.
Figure S4. MWD curves for the synthesis of poly(IBVE)-block-poly(pMeSt) through sequential block copolymerization: (A) [IBVE]<sub>0</sub> = 0.46 M, [IBEA]<sub>0</sub> = 4.0 mM, [Et<sub>1.5</sub>AlCl<sub>1.5</sub>]<sub>0</sub> = 2.5 mM, [SnCl<sub>4</sub>]<sub>0</sub> = 10 mM, [pMeSt]<sub>add</sub> = 0.51 M, [ethyl acetate] = 1.0 M, in toluene at 0 ºC (B) [IBVE]<sub>0</sub> = 0.46 M, [IBEA]<sub>0</sub> = 4.0 mM, [EtAlCl<sub>2</sub>]<sub>0</sub> = 2.5 mM, [SnCl<sub>4</sub>]<sub>0</sub> = 10 mM, [SnCl<sub>4</sub>]<sub>add</sub> = 80 mM, [ethyl acetate] = 1.0 M, in toluene at 0 ºC (C) [IBVE]<sub>0</sub> = 0.76 M, [IBEA]<sub>0</sub> = 4.0 mM, [Et<sub>1.5</sub>AlCl<sub>1.5</sub>]<sub>0</sub> = 5.0 mM, [ethyl acetate] = 50 mM, in CH<sub>2</sub>Cl<sub>2</sub> at 0 ºC. *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: $[\text{pMeSt}]_0 = 0.76 \text{ M}$, $[\text{acetal units}]_0 = 4.0 \text{ mM}$, $[\text{TiCl}_4]_0 = 10 \text{ mM}$, $[\text{SnCl}_4]_0 = 10 \text{ mM}$, $[\text{DTBP}] = 10 \text{ mM}$, $[\text{ethyl acetate}] = 50 \text{ mM}$, in $\text{CH}_2\text{Cl}_2$ at $0 \, ^\circ\text{C}$.
Figure S6. $^1$H NMR spectrum of poly(IBVE-co-DMEVE)-graft-poly(pMeSt) [$M_n$ (GPC) = 5.02 × 10$^4$, $M_w/M_n$ (GPC) = 1.24] after hydrolysis$^a$ (500.16 MHz, CDCl$_3$, 30 ºC).

$^a$ 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(IBVE<sub>110</sub>-co-DMEVE<sub>4</sub>) ($M_n = 1.19 \times 10^4$, $M_w/M_n = 1.13$), (B) poly(pMeSt<sub>88</sub>) ($M_n = 1.04 \times 10^4$, $M_w/M_n = 1.19$), (C) poly(IBVE<sub>138</sub>)-block-poly(pMeSt<sub>144</sub>) ($M_n = 3.81 \times 10^4$, $M_w/M_n = 1.12$) and (D) poly(IBVE<sub>78</sub>-co-DMEVE<sub>4</sub>)-graft-poly(pMeSt<sub>179</sub>) ($M_n = 5.69 \times 10^4$, $M_w/M_n = 1.22$).
Figure S8. $^1$H NMR spectra of poly(IBVE-co-DMEVE)-graft-poly(pMOS) [$M_n$ (GPC) = $6.70 \times 10^4$, $M_w/M_n$ (GPC) = 1.30] (B) and the linear macroinitiator [$M_n$ (GPC) = $0.87 \times 10^4$, $M_w/M_n$ (GPC) = 1.12] (A) (500.16 MHz, CDCl$_3$, 30 ºC).
Figure S9. $^1$H NMR spectra of poly(IBVE-co-DMEVE)-graft-poly(tBOS) \( [M_n \text{ (GPC)} = 13.9 \times 10^4, M_w/M_n \text{ (GPC)} = 1.58] \) (B) and the linear macroinitiator \( [M_n \text{ (GPC)} = 1.69 \times 10^4, M_w/M_n \text{ (GPC)} = 1.10] \) (A) (500.16 MHz, CDCl$_3$, 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, [TiCl₄]₀ = 10 mM, [SnCl₄]₀ = 10 mM, [DTBP] = 10 mM, [ethyl acetate] = 0.50 M, in CH₂Cl₂ at 0 ºC.