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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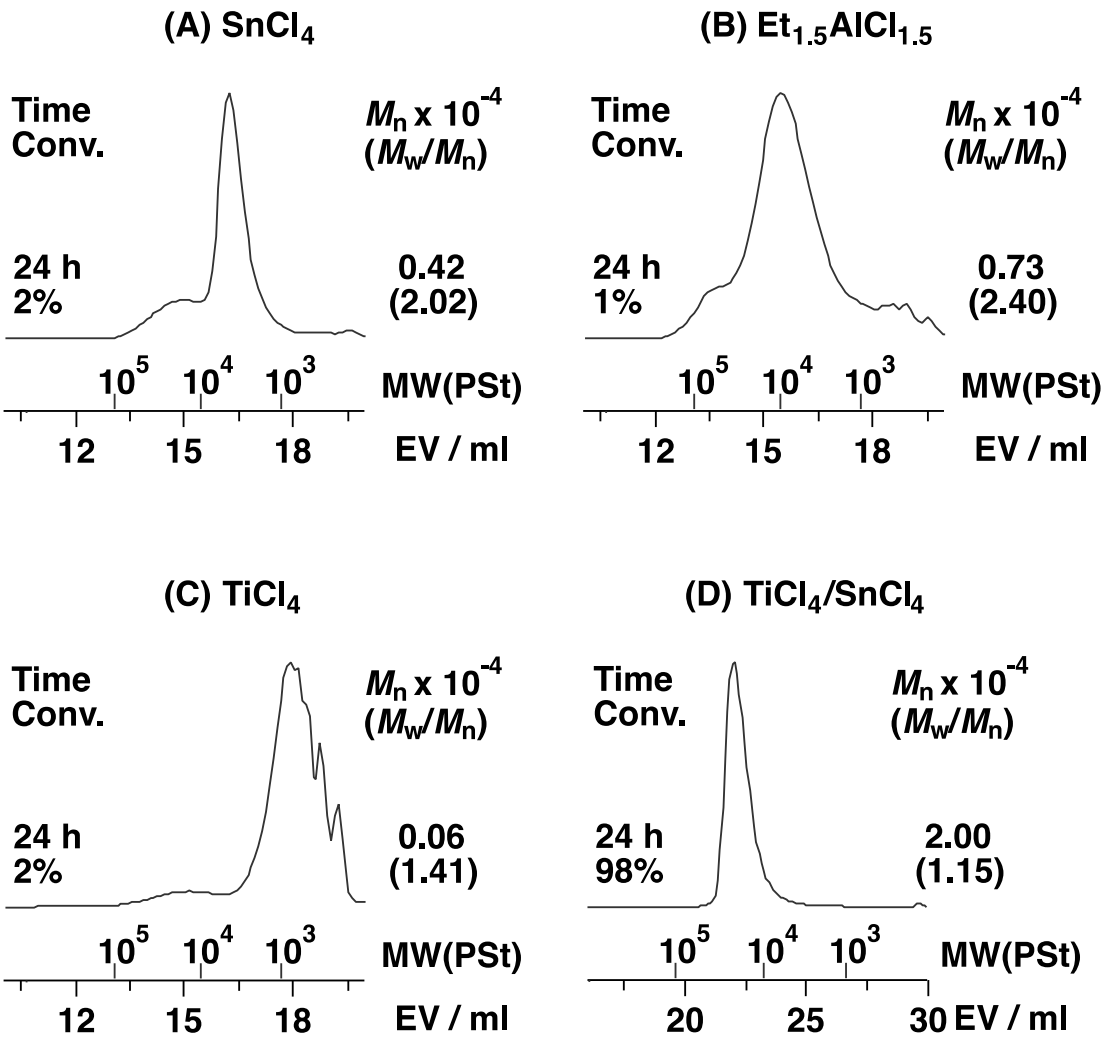

Figure S1. MWD curves for poly(pMeSt)s obtained using the TME/Lewis acid initiating systems: $[pMeSt]_0$ = 0.76 M, $[TME]_0$ = 4.0 mM, $[Lewis\ Acid]_0$ = 20 mM ($Et_{1.5}AlCl_{1.5}$ and $TiCl_4$) or 10 mM ($SnCl_4$), or 5.0/10 mM ($TiCl_4/SnCl_4$), $[DTBP]_0$ = 10 mM, [ethyl acetate] = 50 mM, in CH_2Cl_2 at 0 ºC.

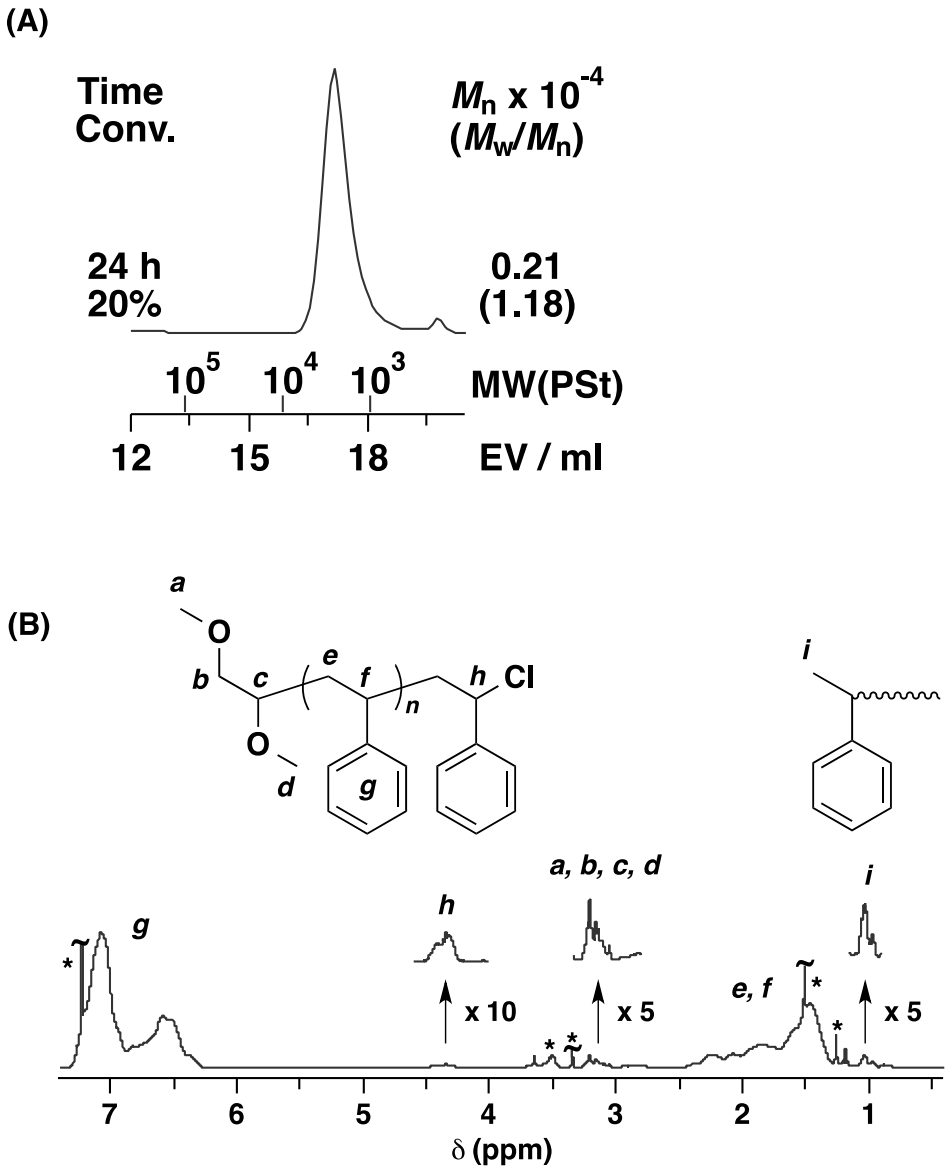

Figure S2. (A) MWD curve of the obtained polystyrene using the TME-$TiCl_4$/$SnCl_4$ initiating system: $[St]_0$ = 0.87 M, $[TME]_0$ = 4.0 mM, $[TiCl_4]_0$ = 5.0 mM, $[SnCl_4]_0$ = 20 mM, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH_2Cl_2 at 0 ºC (B) ^1H NMR spectrum of polystyrene (500.16 MHz, $CDCl_3$, 30 ºC; * solvent, vaseline, water, etc.).

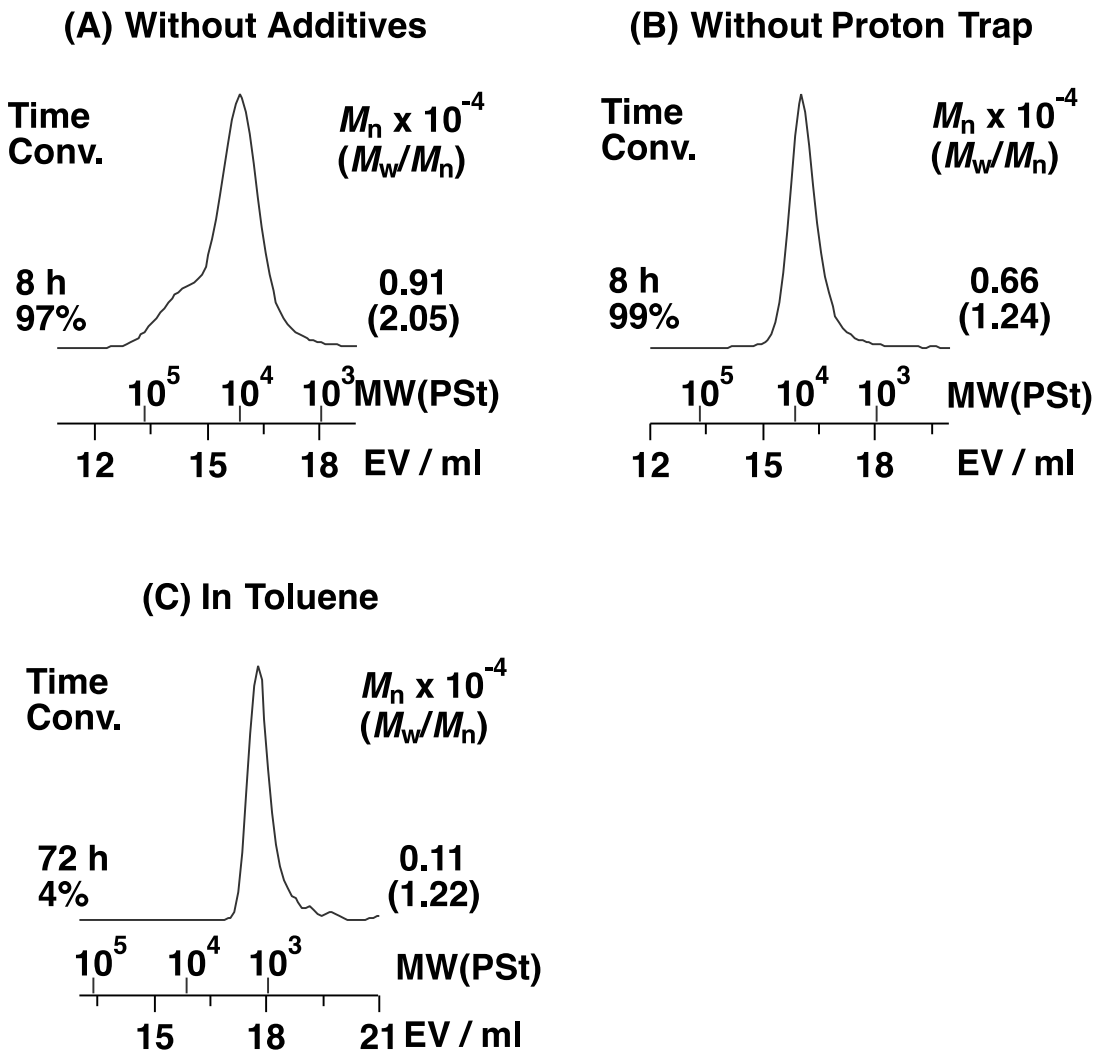

Figure S3. MWD curves for poly(pMeSt)s obtained using the TME-$TiCl_4$/$SnCl_4$ initiating system: $[pMeSt]_0$ = 0.76 M, $[TME]_0$ = 4.0 mM, $[TiCl_4]_0$ = 5.0 mM, $[SnCl_4]_0$ = 10 mM, [DTBP] = 0 (A and B) or 10 mM (C), [ethyl acetate] = 0 (A) or 50 mM (B and C), in CH_2Cl_2 (A and B) or toluene (C) at 0 ºC.

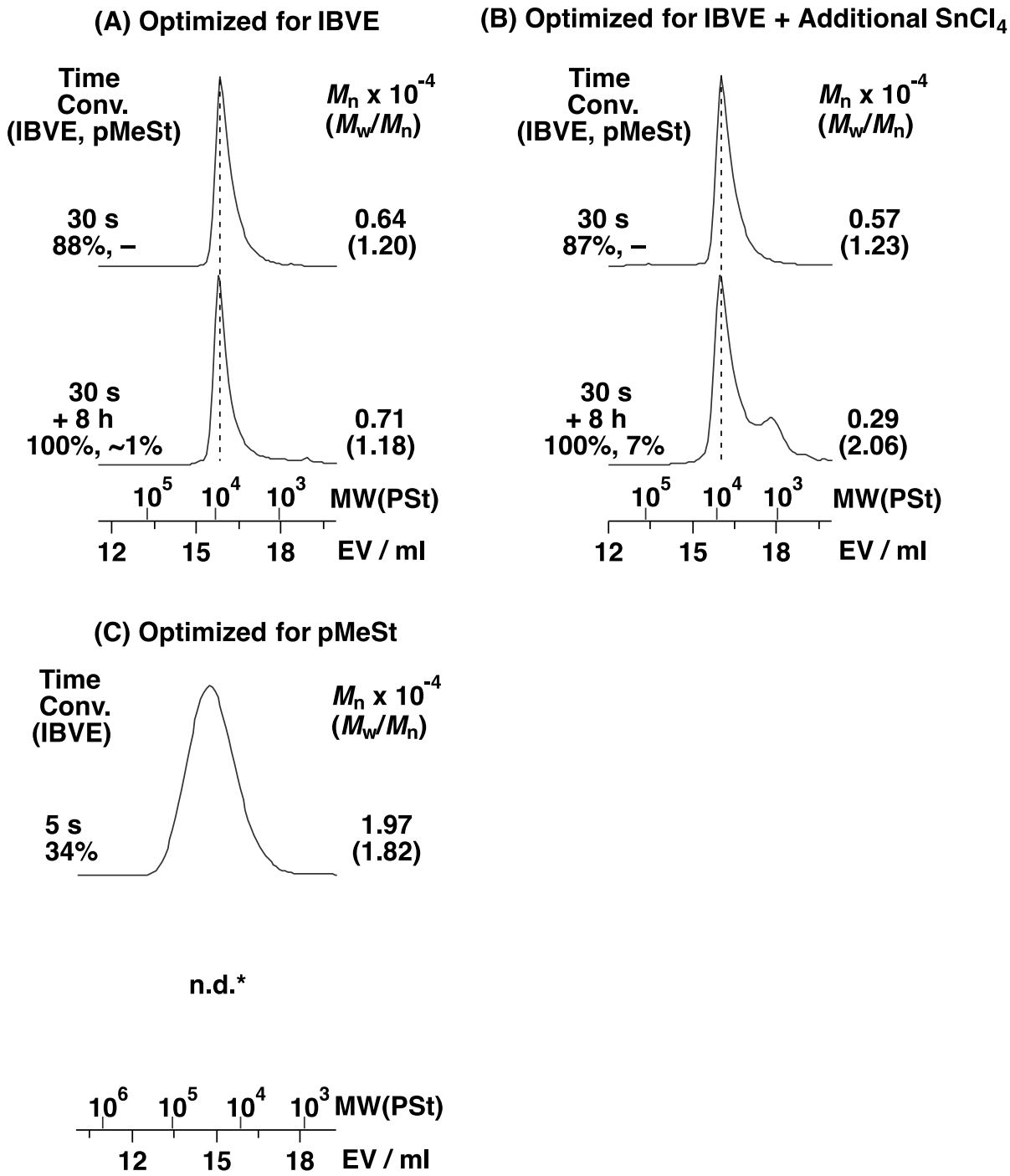

Figure S4. MWD curves for the synthesis of poly(IBVE)-*block*-poly(pMeSt) through sequential block copolymerization: (A) $[IBVE]_0$ = 0.46 M, $[IBEA]_0$ = 4.0 mM, $[Et_{1.5}AlCl_{1.5}]_0$ = 2.5 mM, $[SnCl_4]_0$ = 10 mM, $[pMeSt]_{add}$ = 0.51 M, [ethyl acetate] = 1.0 M, in toluene at 0 ºC (B) $[IBVE]_0$ = 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 ºC (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_2Cl_2 at 0 ºC. *The subsequent addition of pMeSt was not conducted because the first segment was not synthesized precisely.

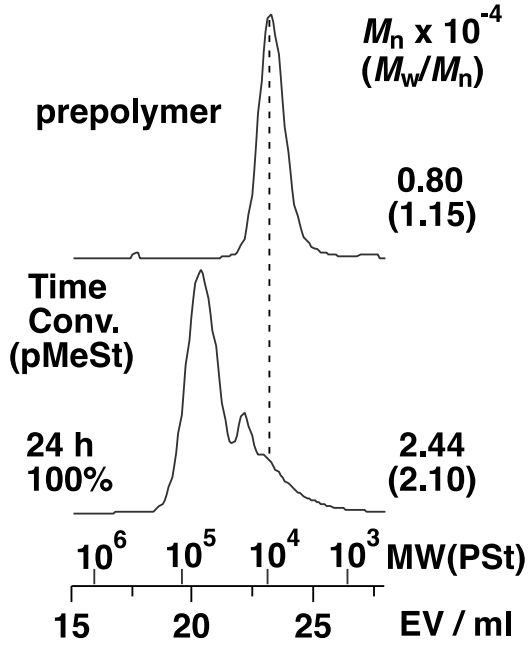

Figure S5. MWD curves for the synthesis of poly(IBVE-*co*-DMEVE)-*graft*-poly(pMeSt) using poly(IBVE-*co*-DMEVE) as a macroinitiator: $[pMeSt]_0$ = 0.76 M, [acetal units]$_0$ = 4.0 mM, $[TiCl_4]_0$ = 10 mM, $[SnCl_4]_0$ = 10 mM, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH_2Cl_2 at 0 ºC.

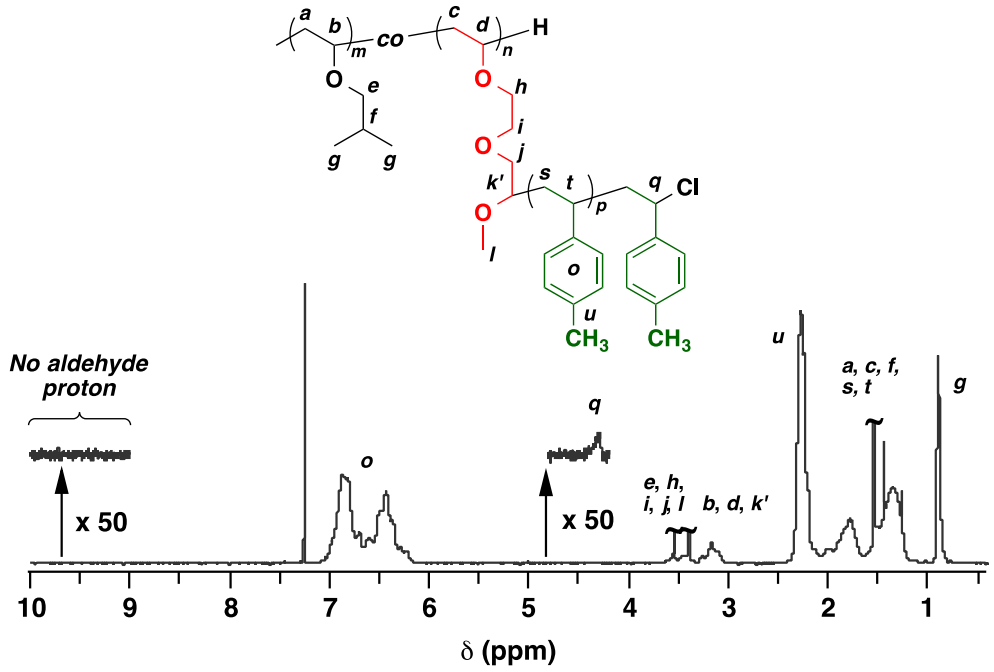

Figure S6. ^{1}H NMR spectrum of poly(IBVE-*co*-DMEVE)-*graft*-poly(pMeSt) [M_n (GPC) = 5.02 × 10^4, M_w/M_n (GPC) = 1.24] after hydrolysis[a] (500.16 MHz, $CDCl_3$, 30 ºC).

[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.

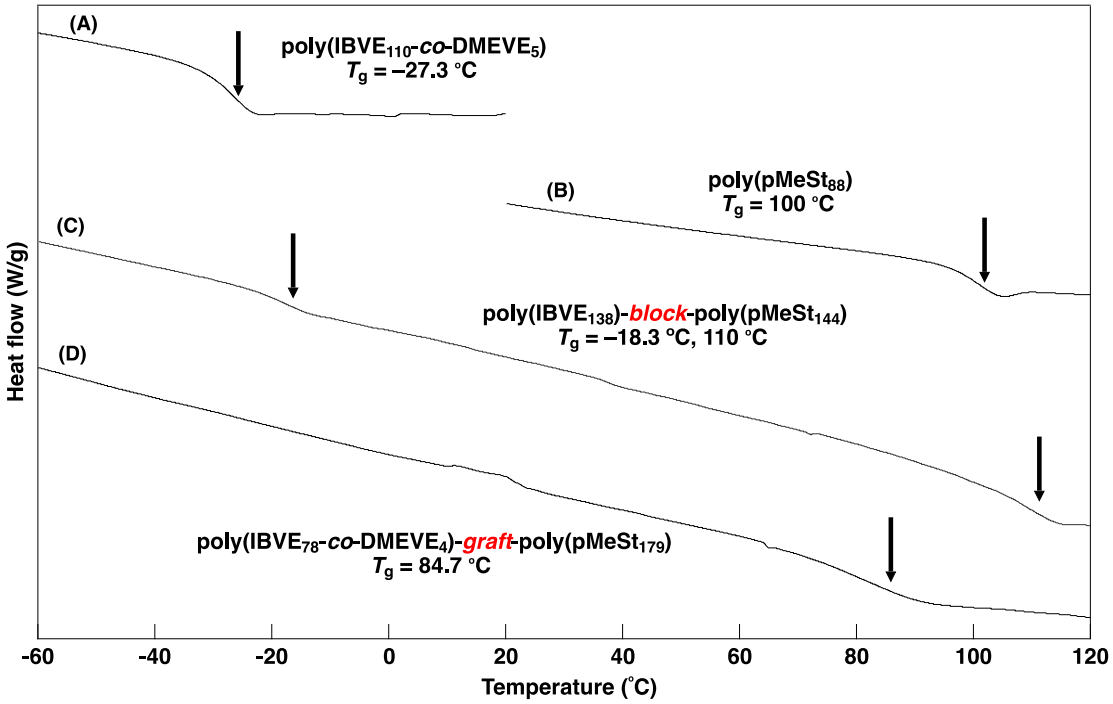

Figure S7. DSC thermograms for (A) poly(IBVE$_{110}$-*co*-DMEVE$_5$) (M_n = 1.19 × 10^4, M_w/M_n = 1.13), (B) poly(pMeSt$_{88}$) (M_n = 1.04 × 10^4, M_w/M_n = 1.19), (C) poly(IBVE$_{138}$)-*block*-poly(pMeSt$_{144}$) (M_n = 3.81 × 10^4, M_w/M_n = 1.12) and (D) poly(IBVE$_{78}$-*co*-DMEVE$_4$)-*graft*-poly(pMeSt$_{179}$) (M_n = 5.69 × 10^4, M_w/M_n = 1.22).

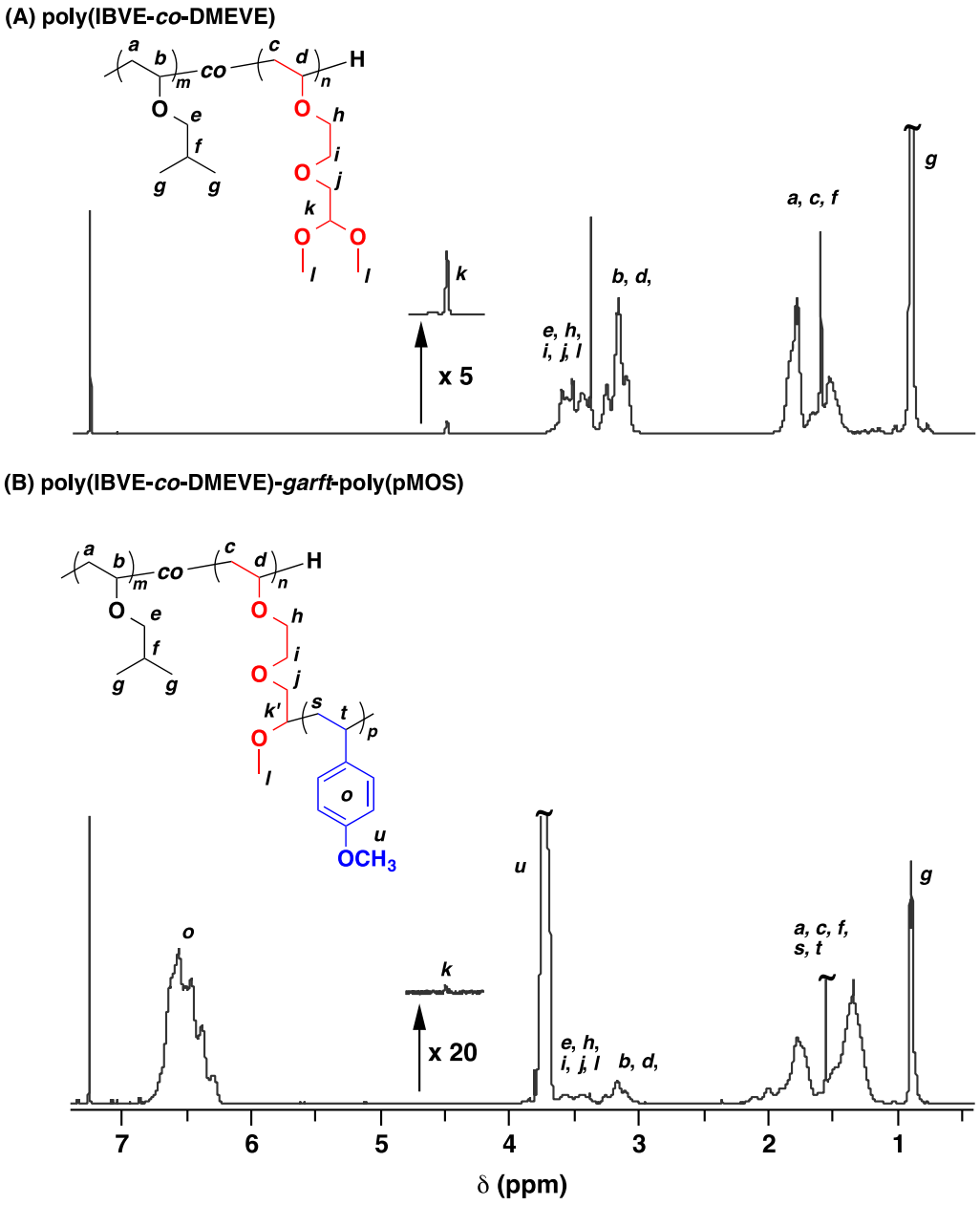

Figure S8. ^{1}H NMR spectra of poly(IBVE-*co*-DMEVE)-*graft*-poly(pMOS) [M_n (GPC) = 6.70 × 10^4, M_w/M_n (GPC) = 1.30] (B) and the linear macroinitiator [M_n (GPC) = 0.87 × 10^4, M_w/M_n (GPC) = 1.12] (A) (500.16 MHz, $CDCl_3$, 30 ºC).

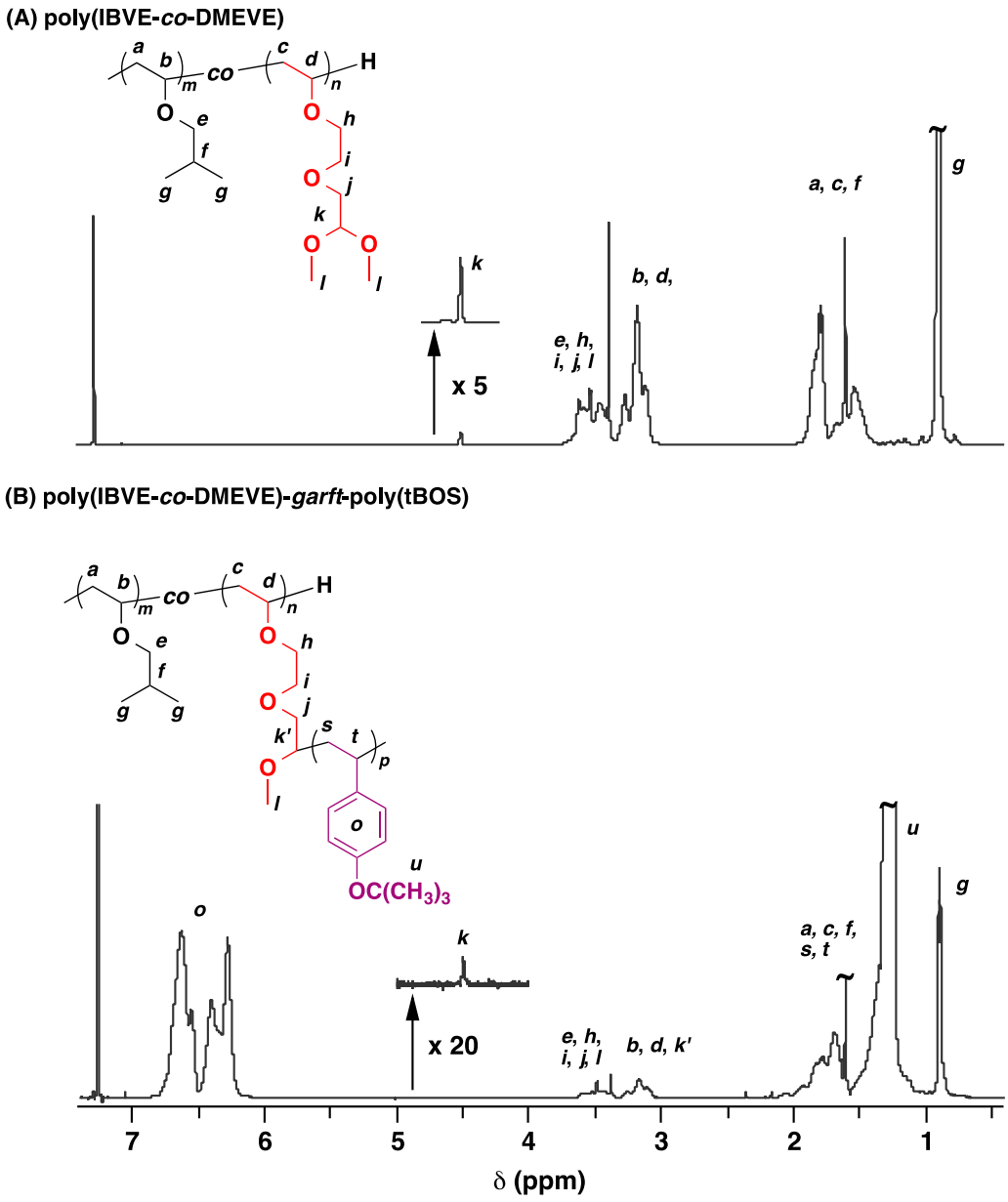

Figure S9. ^{1}H NMR spectra of poly(IBVE-*co*-DMEVE)-*graft*-poly(tBOS) [M_n (GPC) = 13.9 × 10^4, M_w/M_n (GPC) = 1.58] (B) and the linear macroinitiator [M_n (GPC) = 1.69 × 10^4, M_w/M_n (GPC) = 1.10] (A) (500.16 MHz, $CDCl_3$, 30 ºC).

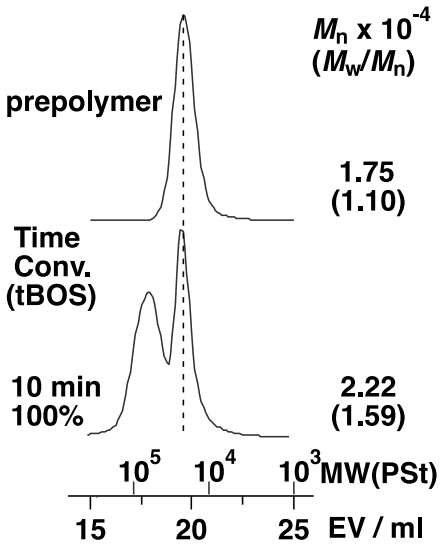

Figure S10. MWD curves for the synthesis of poly(IBVE-*co*-DMEVE)-*graft*-poly(tBOS) using poly(IBVE-*co*-DMEVE) as a macroinitiator: $[tBOS]_0$ = 0.53 M, [acetal units]$_0$ = 4.8 mM, $[TiCl_4]_0$ = 10 mM, $[SnCl_4]_0$ = 10 mM, [DTBP] = 10 mM, [ethyl acetate] = 0.50 M, in CH_2Cl_2 at 0 ºC.