Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

R–Cl/$SnCl_4$/*n*-Bu_4NCl-induced direct living cationic polymerization of naturally-derived unprotected 4-vinylphenol, 4-vinylguaiacol, and 4-vinylcatechol in CH_3CN

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Contents:

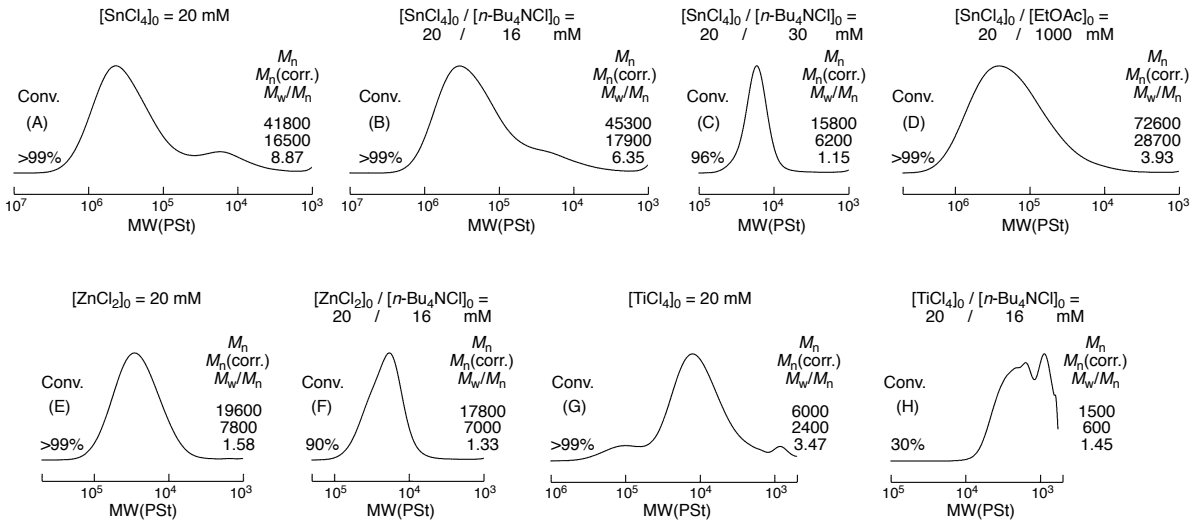

Fig. S1. SEC curves of the polymers obtained in direct cationic polymerization of unprotected pHOS using pMOS–HCl and $MtCl_n$ in the absence and presence of additives in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C: $[pHOS]_0/[pMOS–HCl]_0$ = 500/10 mM; $[SnCl_4]_0$ = 20 mM (A), $[SnCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 20/16 mM (B), $[SnCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 20/30 mM (C), $[SnCl_4]_0/[EtOAc]_0$ = 20/1000 mM (D), $[ZnCl_2]_0$ = 20 mM (E), $[ZnCl_2]_0/[n\text{-}Bu_4NCl]_0$ = 20/16 mM (F), $[TiCl_4]_0$ = 20 mM (G), $[TiCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 20/16 mM (H). M_n(corr.) was determined by SEC using polystyrene standard and the calibration factor (f = 0.396).

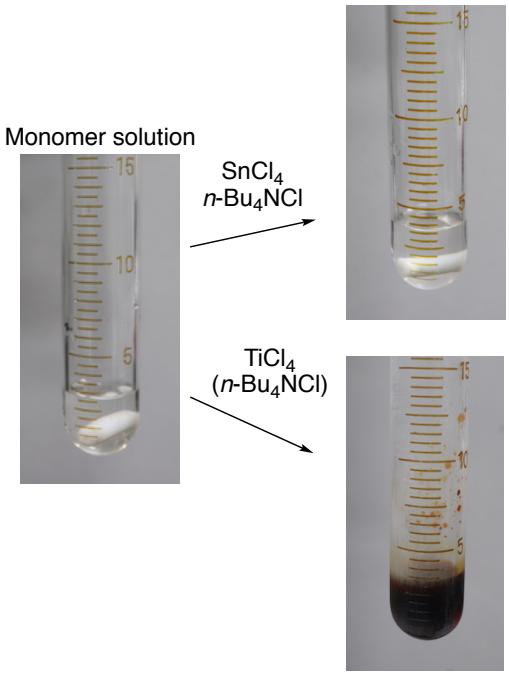

Fig. S2. Reaction mixture of pHOS: $[pHOS]_0/[pMOS–HCl]_0$ = 500/10 mM in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C, $[SnCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 20/30 mM, or $[TiCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 20/30 mM.

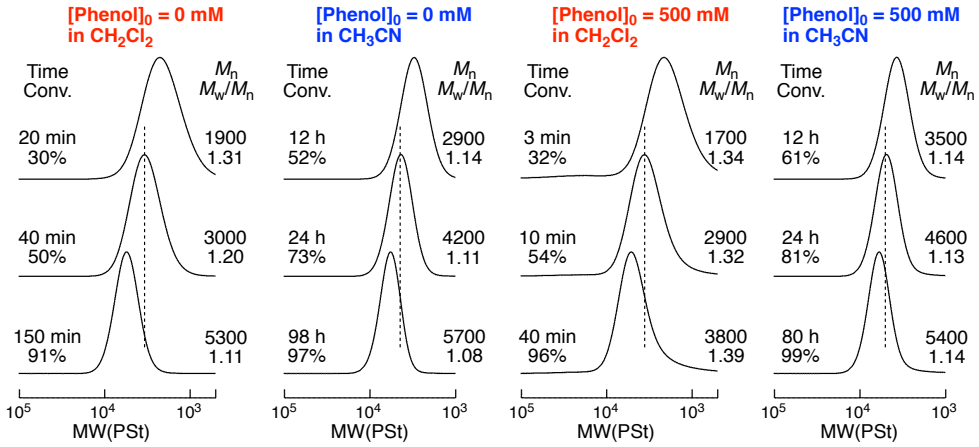

Fig. S3. SEC curves for cationic polymerization of pMOS with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in the absence and presence of phenol: $[pMOS]_0/[pMOS–HCl]_0/[SnCl_4]_0/[n\text{-}Bu_4NCl]_0/[phenol]_0$ = 500/10/10/15/0 or 500 mM in CH_2Cl_2 at –40 °C or $[pMOS]_0/[pMOS–HCl]_0/[SnCl_4]_0/[n\text{-}Bu_4NCl]_0/[phenol]_0$ = 500/10/20/30/0 or 500 mM in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C.

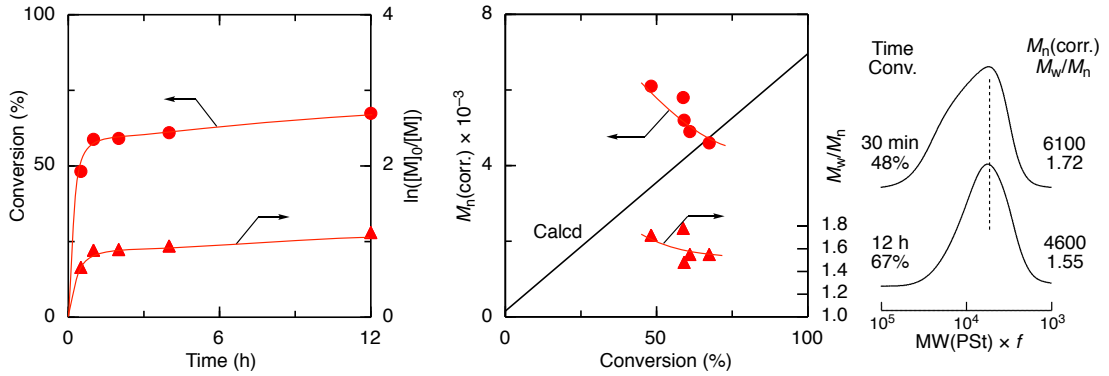

Fig. S4. Time-conversion curve and M_n, M_w/M_n, and SEC curves for direct cationic polymerization of unprotected 4VC with pMOS–OH/BF_3OEt_2 in CH_3CN in the presence of water: $[4VC]_0/[pMOS–HCl]_0/[BF_3OEt_2]_0/[H_2O]_0$ = 200/4.0/2.0/200 mM in CH_3CN at 0 °C. M_n(corr.) was determined by SEC using polystyrene standard and the calibration factor (f = 0.410).

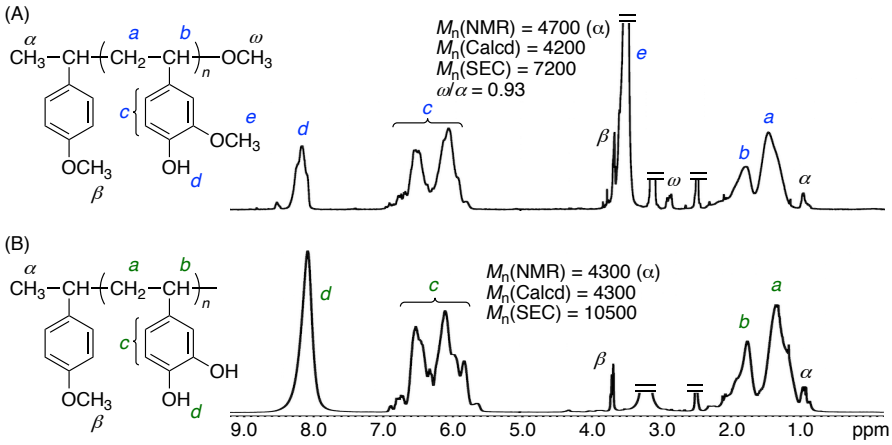

Fig. S5. ^{1}H NMR spectra (DMSO-d_6, 70 °C) of poly(4VG) (A) and poly(4VC) (B) obtained with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C.