Supporting Information for:

In Situ and Readily Prepared Metal Catalysts for Living Cationic Polymerization of Isobutyl Vinyl Ether: Dual-Purpose Salphen as a Ligand Framework for $ZrCl_4$ and an Initiating Proton Source

*Sensho Kigoshi, Arihiro Kanazawa, Shokyoku Kanaoka, and Sadahito Aoshima**

Department of Macromolecular Science, Graduate School of Science, Osaka University,

Toyonaka, Osaka 560-0043, Japan

Contents:

Experimental Section

Materials

Isobutyl vinyl ether (IBVE: TCI; >99.0%), ethyl acetate (Wako; >99.5%), and heptane (Nacalai Tesque; >99.0%) were distilled twice over calcium hydride before use. Toluene (Wako; 99.5%) and dichloromethane (CH_2Cl_2, Wako; 99.9%) were dried using solvent purification columns (Glass Contour). The preparation of 1-(isobutoxy)ethyl chloride [IBVE–HCl; $CH_3CH(O\textit{i}Bu)Cl$] was accomplished via the addition reaction of IBVE with dry HCl, according to the reported method[S1]. Commercially available $SnCl_4$ (Aldrich; 1.0 M solution in heptane), $ZnCl_2$ (Aldrich; 1.0 M solution in diethyl ether), and $TiCl_4$ (Aldrich; 1.0 M solution in dichloromethane) were used without further purification. An $FeCl_3$ stock solution in diethyl ether was prepared from anhydrous $FeCl_3$ (Aldrich; 99.99%). Stock solutions of $AlCl_3$ and $ZrCl_4$ in ethyl acetate were prepared from anhydrous $AlCl_3$ (Aldrich; 99%) and $ZrCl_4$ (Aldrich; 99.99%), respectively. All chemicals except dichloromethane and toluene were stored in brown ampules under dry nitrogen.

Polymerization procedure

The following is a typical procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; blow temperature approximately 450 °C) under dry nitrogen. Toluene, heptane, ethyl acetate, and IBVE were added successively into the tube using dry syringes. In another tube, a metal chloride solution was added to a salphen ligand and ethyl acetate in dichloromethane (or in toluene for Table 1, entry 2), and the solution was kept at 0 °C (or room temperature for Table 1, entries 2 and 3) for at least 30 min to achieve quantitative complexation. The polymerization was initiated by the addition of the complex solution to the monomer solution at the polymerization temperature (or room temperature for Table 1, entry 2). In the case of polymerization reaction at –78 ºC (Table 1, entry 5), toluene, heptane, ethyl acetate, a metal chloride and a salphen ligand were added successively into the tube using dry syringes, and the solution was kept at 0 °C for at least 30 min to achieve quantitative complexation. The polymerization was initiated by the addition of the monomer solution to the complex solution at the polymerization temperature. The reaction was terminated by the addition of methanol containing a small amount of aqueous ammonia solution. The quenched reaction mixture was diluted with hexane and washed successively with dilute hydrochloric acid, aqueous NaOH solution, and water. The organic layer was evaporated under reduced pressure at 50 °C to remove the remaining volatile compounds. The product was dried in vacuo for at least 6 h at room temperature. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport B; GL Sciences Inc.) using heptane as an internal standard.

Characterization

The MWD of the polymers was measured by gel chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel $GM_{HHR–M}$ × 2 or 3 (exclusion limit molecular weight = 4 × 10^6; based size = 5 μm; column size = 7.8 mm I.D. × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; M_n = 577–1.09 × 10^6, $M_w/M_n \leq 1.1$). The NMR spectra were recorded using a JEOL JNM-ECA 500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) and a JEOL JNM-ECA 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C).

Synthesis of salphen ligand [*N,N'* -*o*-phenylene-bis(3,5-di-*tert*-butyl-salicylidene-imine)]

The ligand was prepared using the similar method described in the literature[S2]. A solution of 1,2-diaminobenzene (0.49 g, 4.55 mmol) in methanol (3 mL) was added to a solution of 3,5-di-*tert*-butyl-salicylaldehyde (2.14 g, 9.12 mmol) in methanol (15 mL) while stirring under a nitrogen atmosphere at room temperature. The mixed solution was refluxed for 5 h, and the reaction mixture was then cooled to room temperature. After filtration, the solid fraction was washed twice with cold methanol and dried under reduced pressure. Furthermore, the obtained solid was purified by recrystallization from ethyl acetate to mainly remove residual methanol. The ligand was obtained as a yellow solid (1.01 g, 21%). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 13.51 (2H, s, OH), 8.65 (2H, s, N=C*H*), 7.44 (2H, m, C*H*-phenol), 7.31 (2H, m, C*H*-phenylene), 7.23 (2H, m, C*H*-phenylene), 7.21 (2H, m, C*H*-phenol), 1.43 (18H, s, *t*Bu), 1.32 (18H, s, *t*Bu). ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C): δ 164.7 (N=*C*H), 158.6 (*C*–OH), 142.8 (*ipso*-phenylene), 140.3, 137.2, 118.4 (*ipso*-phenol), 128.2, 127.3, 126.8, 119.8 (phenol and phenylene), 35.1, 34.2 (*C*Me_3), 31.5, 29.5 (C*Me*$_3$).

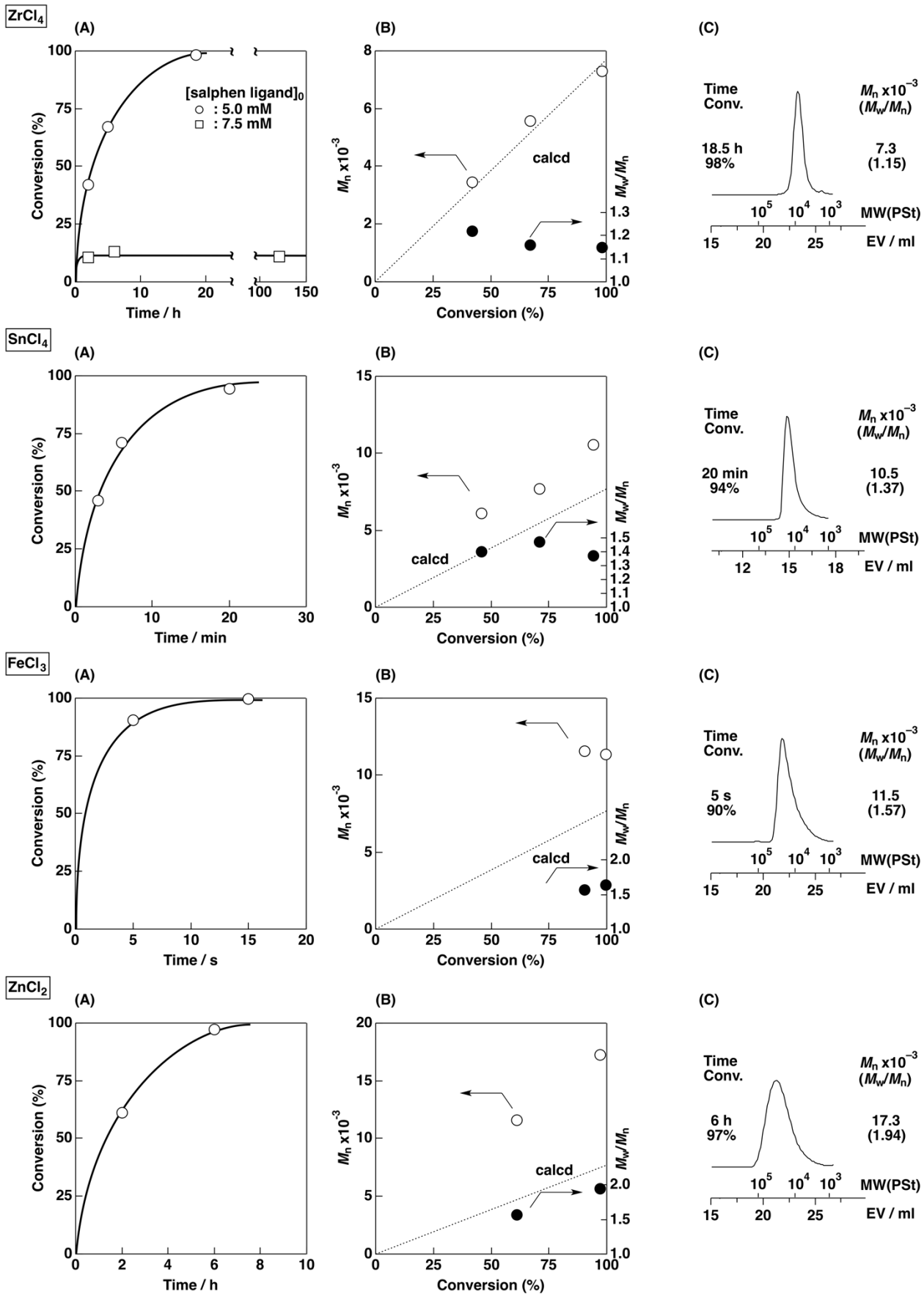

Figure S1. (A) Time–conversion curves for the polymerization, (B) M_n (dotted line: calculated M_n) and M_w/M_n and (C) MWD curves for poly(IBVE)s obtained using the salphen/MCl_n initiating systems ($[IBVE]_0$ = 0.76 M, $[MCl_n]_0$ = 5.0 mM, [salphen ligand]$_0$ = 5.0 mM (circle) or 7.5 mM (square), [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene at 0 ºC).

Notes: The polymerization using $ZrCl_4$ and 1.5 equimolar amounts of the salphen ligand (Figure S1, square) indicated that uncomplexed, free ligand molecules prevented the propagating reaction. The hydroxy group on the ligand possibly reacted with the propagating carbocation but the resulting structure, the acetal chain end having the ligand, was not detected on the ^1H NMR spectra of the products. In the reactions using $SnCl_4$ and $ZnCl_2$, ligand molecules that remained due to insufficient complex formation would have also reacted with the propagating chains, but a direct proof was not obtained similarly. The catalytic solutions for $SnCl_4$, $FeCl_3$, and $TiCl_4$ (entries 7, 8 and 10 in Table 1) afforded heterogeneous systems, and therefore, the polymerizations were conducted using partially soluble catalysts. The heterogeneity would indicate that the complex formation was not quantitative or that several types of complexes were generated.

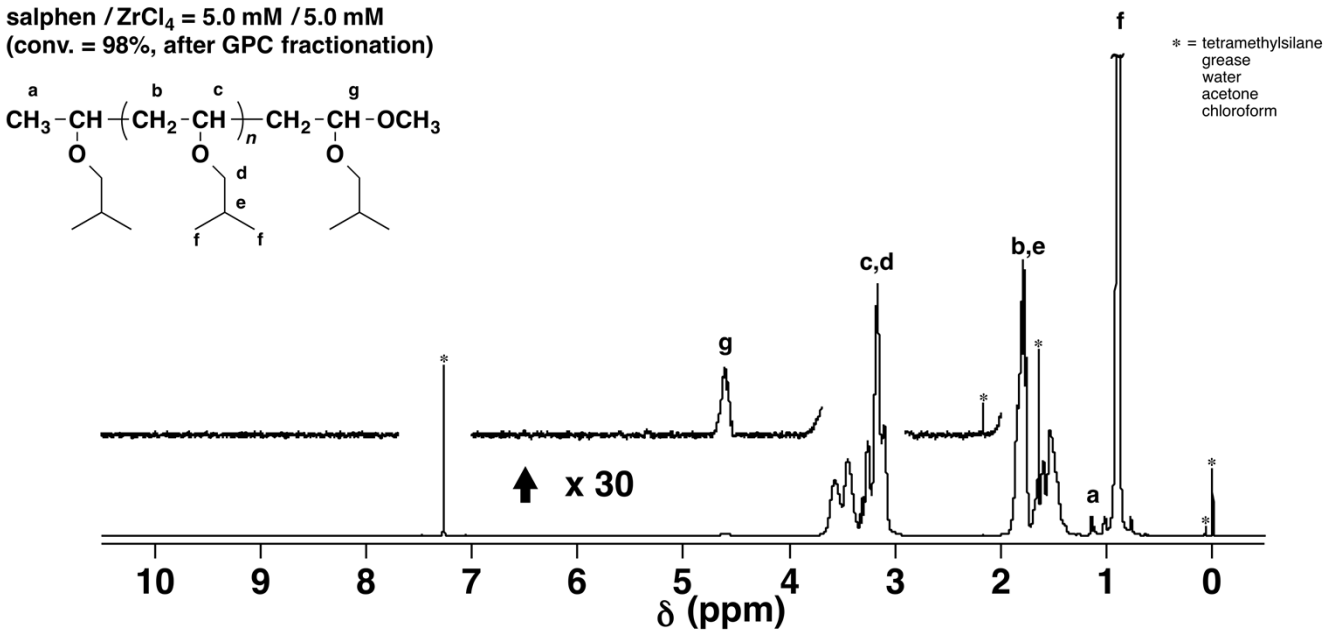

Figure S2. ^{1}H NMR spectrum of poly(IBVE) obtained using the salphen/$ZrCl_4$ initiating system ($[IBVE]_0$ = 0.76 M, $[ZrCl_4]_0$ = 5.0 mM, [salphen ligand]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene at 0 ºC; 500 MHz in $CDCl_3$ at 30 ºC; peak integral ratio: a/g = 3.00/1.02).

Notes: The product polymers obtained using the salphen/$ZrCl_4$ initiating systems at 0 ºC had no irregular structures originating from an undesired reaction, i.e., the dealcoholization of the side chain (three broad peaks are observed at around 5.6, 5.3 and 2.2 ppm) and/or the generation of aldehyde group at chain end (three broad peaks are observed at around 9.8, 4.0 and 2.6 ppm), which was confirmed by ^{1}H NMR (Figure S2 and S3).

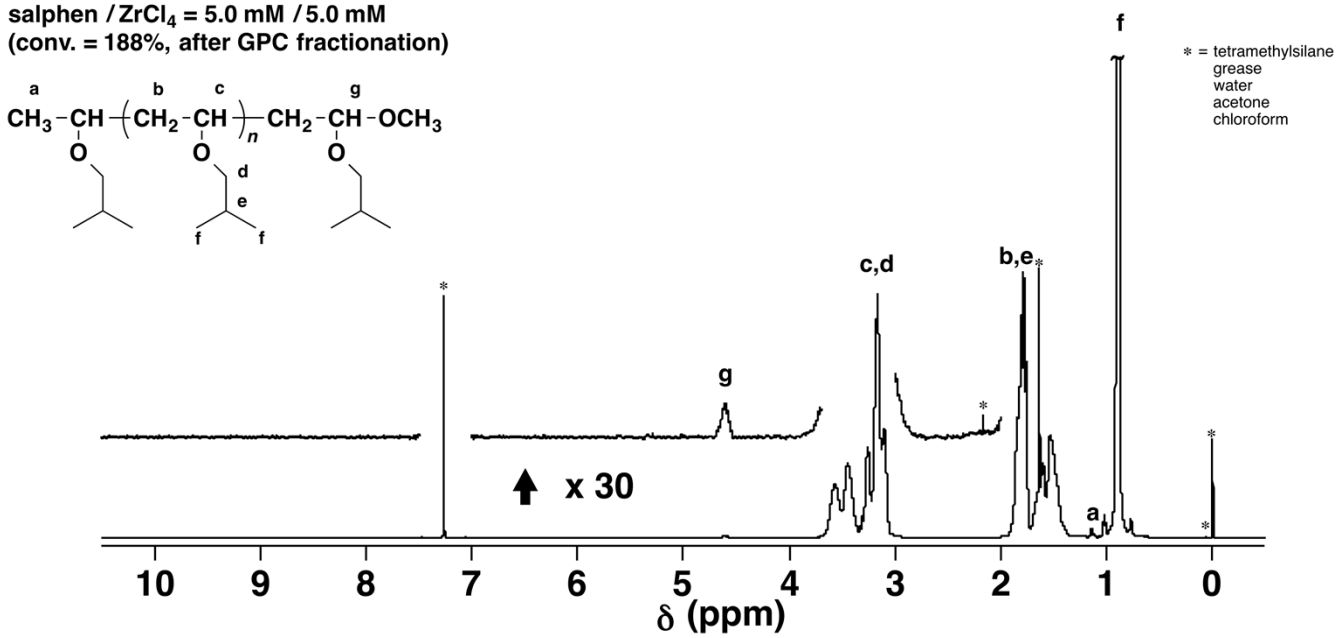

Figure S3. ^{1}H NMR spectrum of poly(IBVE) obtained using the salphen/$ZrCl_4$ initiating system ($[IBVE]_0$ = $[IBVE]_{added}$ = 0.76 M, $[ZrCl_4]_0$ = 5.0 mM, [salphen ligand]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene at 0 ºC; 500 MHz in $CDCl_3$ at 30 ºC; peak integral ratio: a/g = 3.0/1.03).

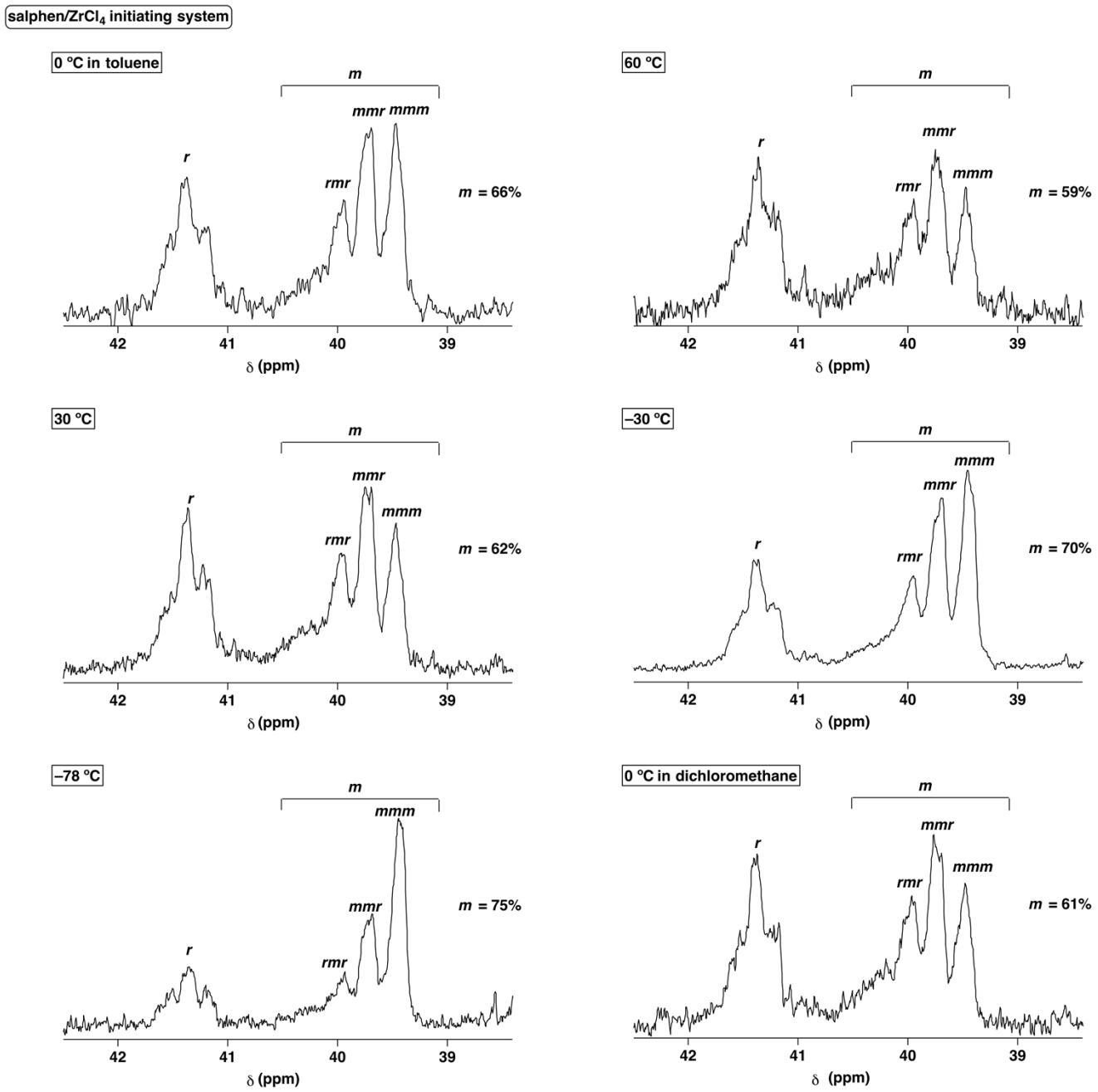

Figure S4. ^{13}C NMR spectra of poly(IBVE)s obtained using the salphen/MCl_n initiating systems ($[IBVE]_0$ = 0.76 M, $[MCl_n]_0$ = 5.0 mM, [salphen ligand]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene at various conditions; 125 MHz for $ZrCl_4$, $FeCl_3$ and $ZnCl_2$ and 100 MHz for $SnCl_4$ in $CDCl_3$ at 30 ºC).

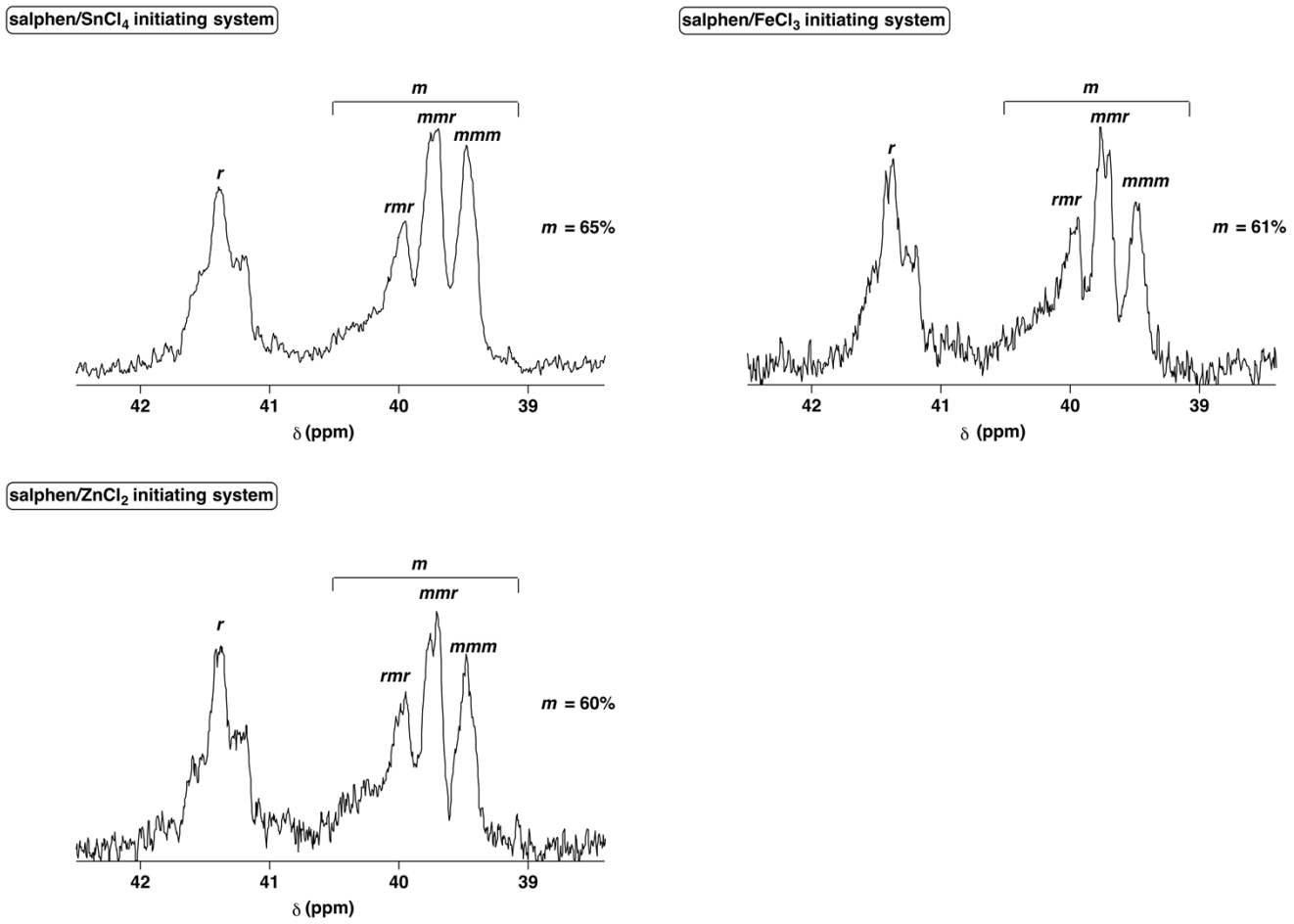

Figure S4. (*continued*)

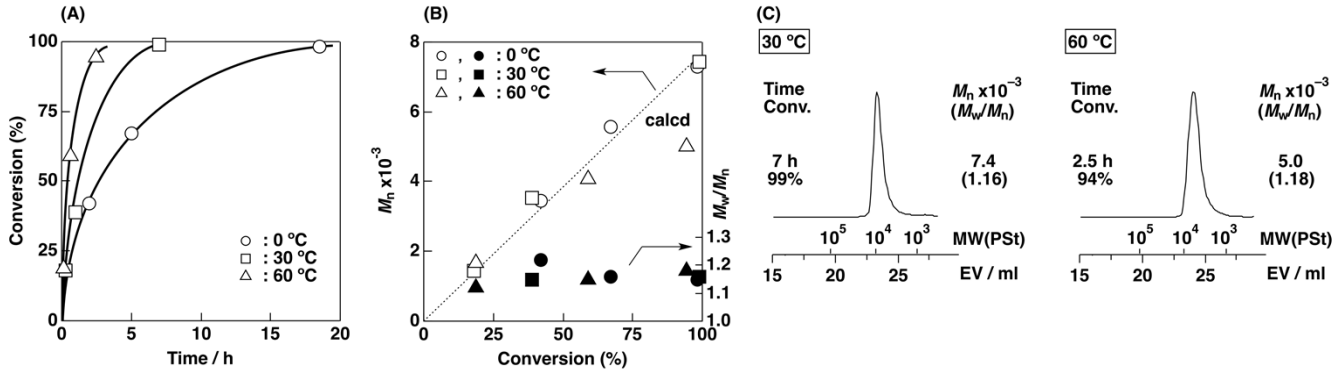

Figure S5. (A) Time–conversion curves for the polymerization, (B) M_n (dotted line: calculated M_n) and M_w/M_n and (C) MWD curves for poly(IBVE)s obtained using the salphen/$ZrCl_4$ initiating systems at 0, 30, or 60 ºC ($[IBVE]_0$ = 0.76 M, $[ZrCl_4]_0$ = 5.0 mM, [salphen ligand]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene).

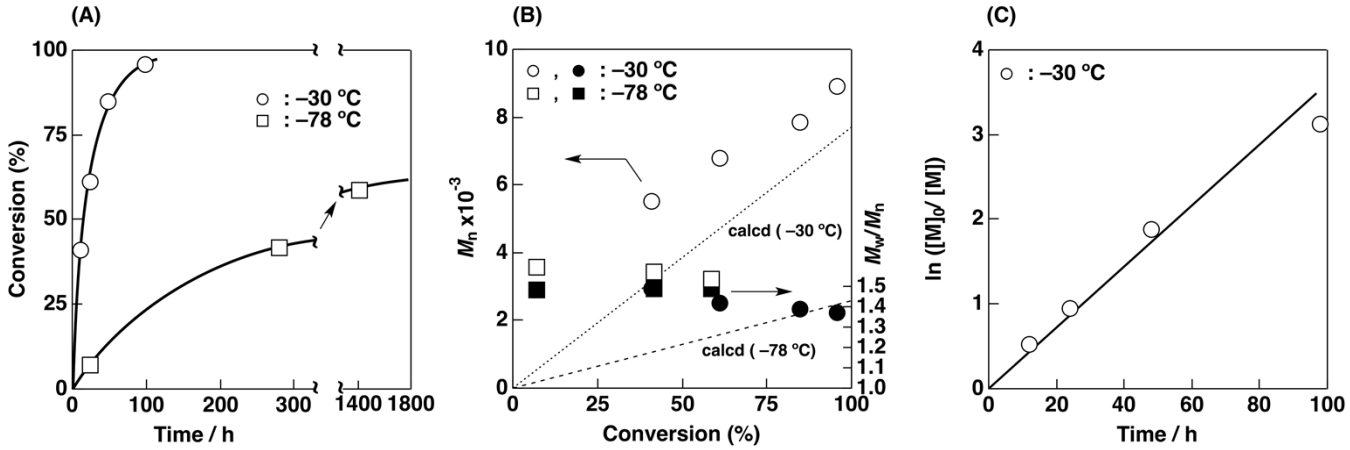

Figure S6. (A) Time–conversion curves, (B) M_n (dotted line: calculated M_n) and M_w/M_n for poly(IBVE)s, and (C) ln([M]$_0$/[M])–time plots for the polymerization using the salphen/$ZrCl_4$ initiating systems at –30 or –78 ºC ([IBVE]$_0$ = 0.76 M, [$ZrCl_4$]$_0$ = 5.0 or 15 mM, [salphen ligand]$_0$ = 5.0 or 15 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene).

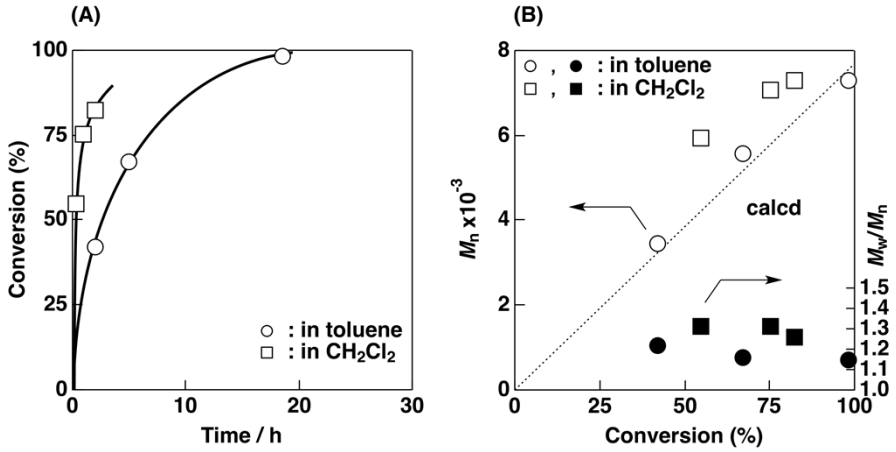

Figure S7. (A) Time–conversion curves for the polymerization and (B) M_n (dotted line: calculated M_n) and M_w/M_n for poly(IBVE)s obtained using the salphen/$ZrCl_4$ initiating system in toluene or dichloromethane ([IBVE]$_0$ = 0.76 M, [$ZrCl_4$]$_0$ = 5.0 mM, [salphen ligand]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % at 0 ºC).

Notes: The polymerization in dichloromethane, a polar solvent, at 0 °C (Table 1, entry 6) proceeded at a much higher rate than in toluene, similar to polymerizations with other common catalysts. In addition, the difference was most likely observed because the active–dormant equilibrium in dichloromethane shifted slightly more towards the active species during the polymerization reaction, producing a polymer with a slightly broader MWD.

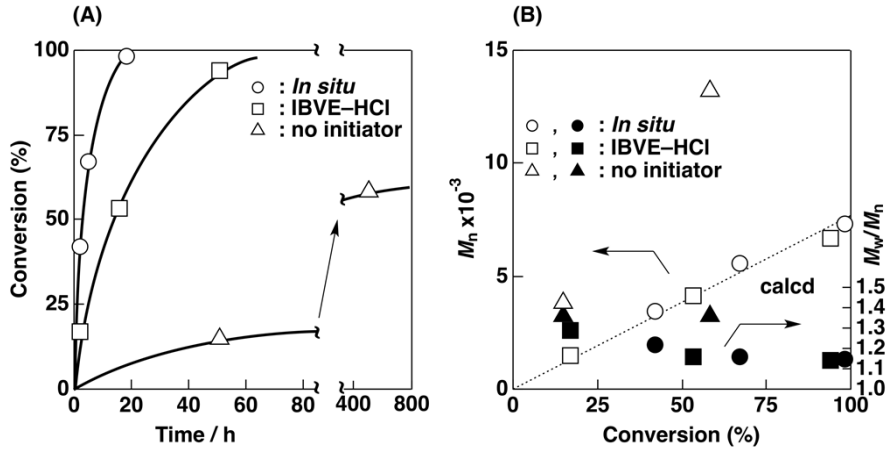

Figure S8. (A) Time–conversion curves for the polymerization and (B) M_n (dotted line: calculated M_n) and M_w/M_n for poly(IBVE)s obtained using the isolated Zr(salphen)Cl_2 (square and triangle) or the salphen/$ZrCl_4$ initiating system (circle) ([IBVE]$_0$ = 0.76 M, [Zr(salphen)Cl_2]$_0$ = 5.0 mM (square and triangle) or [$ZrCl_4$]$_0$ = [salphen ligand]$_0$ = 5.0 mM (circle), [IBVE–HCl]$_0$ = 0 mM (circle and triangle) or 10 mM (square), [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % at 0 ºC).

Notes: After the salphen complex was generated by mixing the salphen ligand and $ZrCl_4$ in dichloromethane, similar to the method described above, the solvents were evaporated under reduced pressure. The dried salphen complex was used as a catalyst without further purification. The reaction without IBVE–HCl resulted in very slow polymerization (Figure S8), suggesting that almost all of HCl was removed during the catalyst isolation process.

The polymerization rate with the isolated salphen complex system was smaller than the rate with the one prepared in situ. The ^{1}H NMR analysis of the isolated salphen complex (Figure S9) indicated that this complex had several isomers[S3,S4]. The catalytic activities of these isomers likely differ from each other. The details of the relationship between the structures of the complexes and their catalytic activities will be discussed in a forthcoming study.

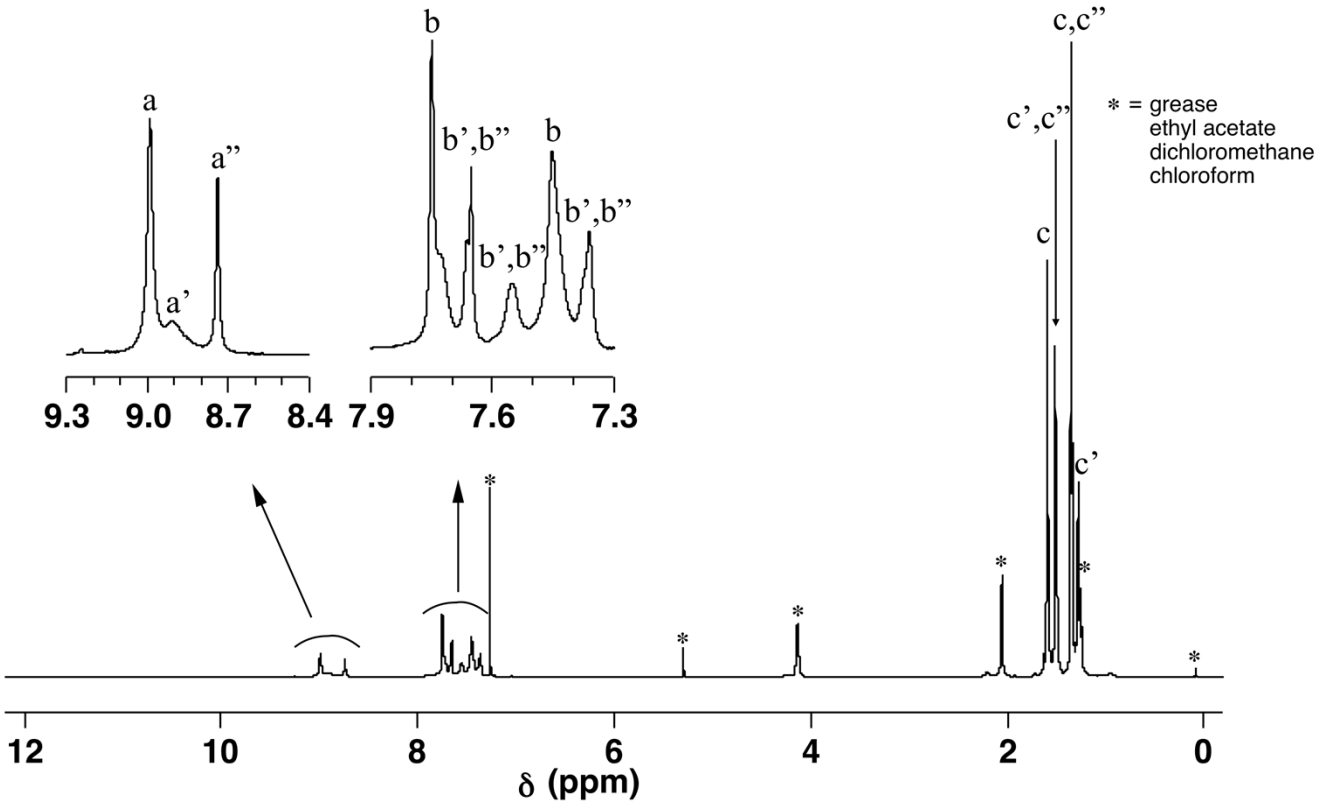

Figure S9. ^{1}H NMR spectrum of the isolated Zr(salphen)Cl_2 by evaporation {a, a’ and a” shows a signal of the methine proton of N=C*H*, b, b’ and b” shows a signal of the phenyl protons, and c, c’ and c” shows a signal of the protons of *t*Bu groups: signals of a, b and c are likely assigned to a *trans* isomer of Zr(salphen)Cl_2, signals of a’, b’ and c’ are likely assigned to a α-*cis* isomer of Zr(salphen)Cl_2, and signals of a”, b” and c” are likely assigned to an H_2O-coordinating Zr(salphen)Cl_2 complex[S3,S4]}.

Reference

S1. T. Higashimura, M. Kamigaito, M. Kato, T. Hasebe and M. Sawamoto, *Macromolecules*, 1993, **26**, 2670–2673.

S2. M. Sanz, T. Cuenca, M. Galakhov, A. Grassi, R. K. J. Bott, D. L. Hughes, S. J. Lancaster and M. Bochmann, *Organometallics*, 2004, **23**, 5324–5331.

S3. M. Sanz, T. Cuenca, C. Cuomo and A. Grassi, *J. Organomet. Chem.*, 2006, **691**, 3816–3822.

S4. M. Wang, H. Zhu, D. Huang, K. Jin, C. Chen and L. Sun, *J. Organomet. Chem.*, 2004, **689**, 1212–1217.