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Supporting Information

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Highly Controlled Living Radical Polymerization through Dual Activations of Organobismuthines

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General. All reaction conditions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon atmosphere. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for a $CDCl_3$ or DMSO-d_6 solution of a sample. ^{1}H NMR spectra are reported in parts per million (δ) from internal tetramethylsilane or residual solvent peak, and ^{13}C NMR from solvent peak. IR spectra (absorption) are reported in cm^{-1}. High resolution mass spectra (HRMS) were obtained under electron impact ionization conditions. MALDI-TOF mass spectra were obtained in the reflection mode and at 20 kV acceleration voltage. Samples were prepared from a THF solution by mixing sample (1 mg/mL), dithranol (10 mg/mL), and sodium trifluoroacetate (1 mg/mL) in a ratio of 5:1:1. The gel permeation chromatography (GPC) was performed two linearly connected polystyrene mixed gel columns, which were calibrated with polystyrene and poly(methyl methacrylate) standards. Chloroform was used as an eluant for polystyrene (PSt), poly(methyl methacrylate) (PMMA), and poly(butyl acrylate) samples, and 0.01 mol L^{-1} lithium chloride solution of DMF for poly(*N*-isopropyl acrylamide) and poly(*N*-vinylpyrroridone) samples.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and were used as received. Styrene, methyl methacrylate, butyl acrylate, and *N*-vinylpyrrolidone were washed with 5% aqueous sodium hydroxide solution and were distilled over calcium hydride under reduced pressure and stored under nitrogen atmosphere. *N*-isopropyl acrylamide was recrystalized from hexane and stored in a refrigerator. 2,2’-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored in a refrigerator. DMF was distilled from CaH_2 and stored under nitrogen atmosphere.

Preparation of 2-diphenylbismuthanyl-2-methylpropionitrile (1b). Isobutyronitrile (1.1 mL, 12 mmol) in THF (10 mL) was added to a solution of lithium diisopropylamide, which was prepared by adding *n*-butyllithium (8.1 mL, 1.49 M in hexane, 12 mmol) to a solution of diisopropylamine (1.7 mL, 12 mmol) in THF (10 mL) at -78 ^{o}C, and the resulting solution was stirred at this temperature for 0.5 h. Diphenylbismuthanyl bromide[1] (4.43 g, 10 mmol) in THF (50 mL) was added to this solution, and the resulting mixture was stirred for 0.5 h at this temperature. The reaction was quenched by addition of saturated and degassed brine, and water layer was extracted by syringe. The resulting organic phase was dried by addition of magnesium sulfate, and passed through a pad of Celite under a nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was purified by recrystallization from diethyl ether to afford the titled product as pale yellow crystals (2.20 g, 51%). ^{1}H NMR (DMSO-d$_6$, 400 MHz) 1.86 (s, 6H, BiCH_3), 7.39 (tt, *J* = 1.2 Hz, 7.4 Hz, 2H, ArH), 7.55 (tt, *J* = 1.2 Hz, 7.4 Hz, 4H, ArH), 7.90 (dt, *J* = 1.2 Hz, 7.4 Hz, 2H, ArH); ^{13}C NMR (DMSO-d$_6$, 100 MHz) 24.66, 27.33, 127.71, 128.04, 130.55, 136.34, 164.73; HRMS (EI) *m/z*: Calcd for $C_{16}H_{16}NBi$ (M)$^+$, 431.1086; Found 431.1058; IR (C_6H_6) 703, 1617, 1807, 1822, 2210, 3013, 3100.

Tributyltin hydride reduction of 1a. A solution of **1a** (34.0 mg, 0.10 mmol), tributyltin hydride (32.1 mg, 0.11 mmol), AIBN (1.6 mg, 0.01 mmol), and 5 μl tetrachloroethane (as internal standard) in 0.6 ml C_6D_6 in a sealed NMR tube was heated at 80 ^{o}C for 1 h. The ^{1}H NMR spectra, taken before and after heating, indicated that **1a** quantitatively converted into the methyl isobutyrate [^{1}H NMR (400 MHz) 1.01 (d, *J* = 6.8 Hz, 6 H), 2.31 (hept, *J* = 6.9 Hz, 1 H), 3.32 (s, 3 H)]. The addition of commercially available methyl isobutyrate (ca. 0.3 mmol) to the unsealed NMR tube increased the peak intensity of its all characteristic peaks. No appearance of the methyne proton at 2.40 ppm was observed when tributyltin deuteride was used instead of tributyltin hydride.

Reaction of 1a with TEMPO. A solution of **1a** (34 mg, 0.10 mmol) and TEMPO (18.75 mg, 0.12 mmol) in 0.6 mL C_6D_6 in a sealed NMR tube was heated at 80 °C for 1 h. The ^{1}H NMR spectra indicated 83 % formation of TEMPO-adduct **2a**[2] and 7 % of methyl methacrylate together with 10 % of unreacted **1a**. Pure **2a** was isolated by preparative GPC. ^{1}H NMR (400 MHz, CDCl$_3$) 0.99 (s, 6H), 1.14 (s, 6H), 1.23-1.5 (m, 6H), 1.47 (s, 6H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) 17.07, 20.43, 24.46, 33.37, 40.58, 51.75, 59.53, 81.12, 176.53; HRMS (EI) *m/z*: Calcd for $C_7H_{15}O_2Bi$ (M)$^+$, 257.1991; Found 257.1994.

Typical procedure of polymerization of styrene. A solution of styrene (1.04 g, 10 mmol) and **1a** (41 μL, 0.1 mmol) was heated at 100 °C for 4 h with stirring under nitrogen atmosphere in a glove box. A small portion of the reaction mixture was taken and dissolved in CDCl$_3$. The conversion of monomer (96%) was determined by ^{1}H NMR. The rest of reaction mixture was dissolved in CHCl$_3$ (4 mL) and poured into a vigorously stirred methanol (200 mL). The product was collected by filtration and dried under reduced pressure at 40 °C to give 1.013 g of polystyrene. The number averaged molecular weight (M_n = 10,500) and the polydispersity index (PDI = 1.07) were determined by GPC calibrated with polystyrene standards.

GPC traces of each experiments using **1a** by changing styrene/**1a** ratio are shown (Figure S1).

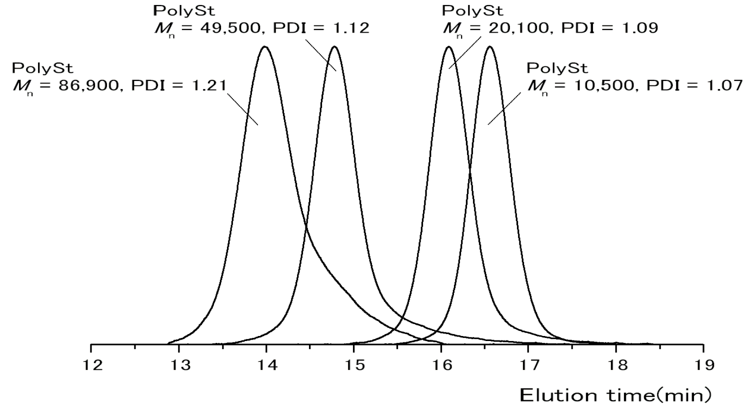


Figure S1. GPC traces of polystyrene samples prepared by varying styrene/**1a** ratio

End-deuteration. A solution of styrene (1.04 g, 10 mmol) and **1a** (65 μL, 0.33 mmol) was heated at 100 °C for 3 h with stirring under nitrogen atmosphere in a glove box. The resulting solid was dissolved by adding α,α,α-trifluoromethylbenzene (4 mL) at room temperature. Tributyltin deuteride (134 μL, 0.45mmol) and AIBN (5.42 mg, 0.03 mmol) was added, and the resulting mixture was stirred at 80 ^{o}C for 1 h. The reaction mixture was poured into a vigorously stirred methanol (200 mL). The product was collected by filtration and dried under reduced pressure at 40 °C to give 1.06 g of polystyrene (100% yield). Analytical GPC indicated that the polymer formed with M_n = 2900 and PDI = 1.09. The polymer was further purified by preparative GPC (to remove residual tin compounds) for MALDI-TOF MS analysis (Figure S2). The MS analysis indicated that the polymer formed with M_n = 3420 and PDI = 1.03.

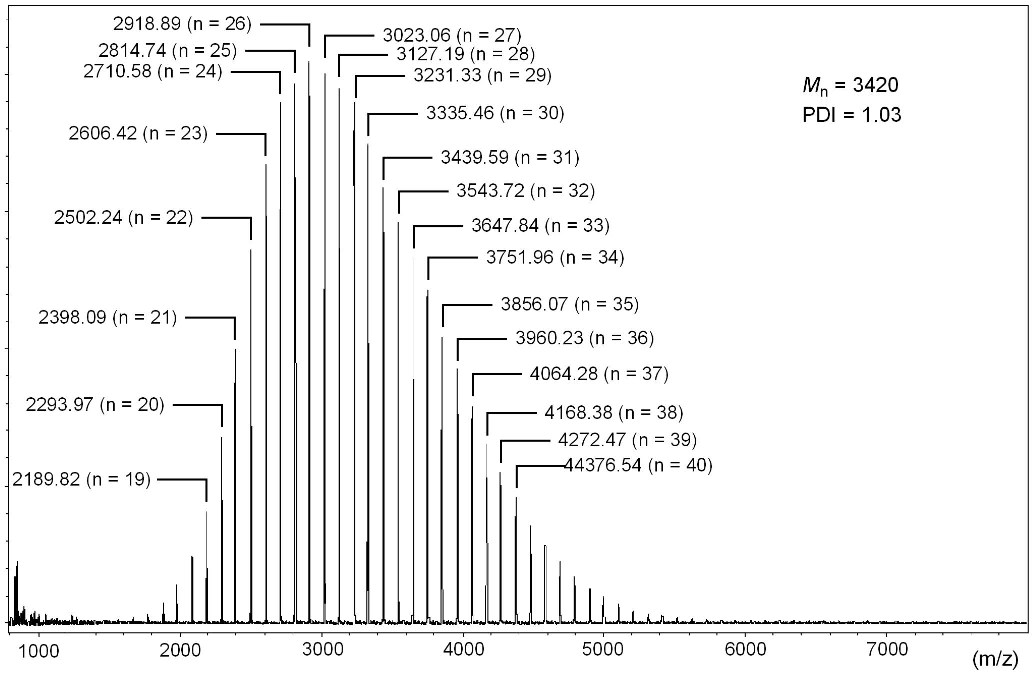


Figure S2. TOF-MS spectra of end-deuterated polystyrene. The molecular ions were observed as silver ion adducts [$m/z = (M + \mathrm{Ag})^+$]. Molecular weight ($M_n$) and polydispersity (PDI) were directly obtained by MS spectra.

Typical procedure of polymerization of methyl methacrylate. A solution of methyl methacrylate (1.00 g, 10 mmol) and **1a** (41 μL, 0.1 mmol) was heated at 100 °C 3 h with stirring under nitrogen atmosphere in a glove box. A small portion of the reaction mixture was withdrawn and dissolved in $CDCl_3$. The conversion of monomer (94%) was determined by ^{1}H NMR. The rest of reaction mixture was dissolved in $CHCl_3$ (4 mL) and poured into a vigorously stirred hexane (200 mL). The product was collected by filtration and dried under reduced pressure at 40 °C. The number averaged molecular weight (M_n = 9900) and the polydispersity index (PDI = 1.13) were determined by GPC calibrated with poly(methyl methacrylate) standards.

Correlation of M_n and amount of methyl methacrylate used of each experiments using **1a** by changing methyl methacrylate/**1a** ratio are shown (Figure S3).

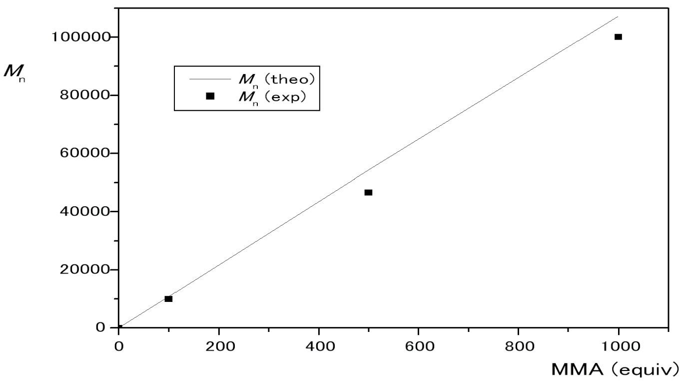


Figure S3. Correlation of experimental and theoretical molecular weight (M_n) of poly(methyl methacrylate) in the bulk polymerization of methyl methacrylate with **1a** as a function of the amount of methyl methacrylate used (100 – 1000 equiv).

Typical procedure of polymerization of *n*-butyl acrylate. A solution of *n*-butyl acrylate (1.28 g, 10 mmol), mediator **1a** (41 μL, 0.1 mmol), and AIBN (3.2 mg, 0.02 mmol) was heated at 60 °C for 3 h with stirring under nitrogen atmosphere in a glove box. A small portion of the reaction mixture was withdrawn and dissolved in $CDCl_3$. The conversion (97%) of monomer was determined by ^1H NMR. After the volatile materials were removed under reduced pressure, the number averaged molecular weight (M_n = 11100) and the polydispersity index (PDI = 1.10) were determined by GPC calibrated with poly(methyl methacrylate) standards.

Correlation of M_n and amount of butyl acrylate used of each experiments using **1a** by changing methyl methacrylate/**1a** ratio are shown (Figure S4).

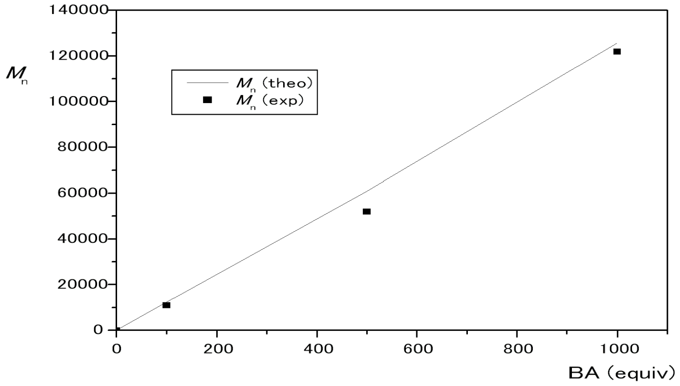


Figure S4. Correlation of experimental and theoretical molecular weight (M_n) of poly(*n*-butyl acrylate) in the bulk polymerization of n-butyl acrylate with **1a** as a function of the amount of *n*-butyl acrylate used (100 – 1000 equiv).

Typical procedure of polymerization of *N*-isopropylacrylamide. A solution of *N*-isopropylacrylamide (0.566 g, 5 mmol), mediator **1a** (21 mL, 0.05 mmol), and AIBN (1.6 mg, 0.01 mmol) in DMF (0.5 mL) was heated at 60 °C for 2 h with stirring under nitrogen atmosphere in a glove box. A small portion of the reaction mixture was withdrawn and dissolved in $CDCl_3$. The conversion of monomer (94%) was determined by ^{1}H NMR. The rest of reaction mixture was dissolved in $CHCl_3$ (4 mL) and poured into a vigorously stirred hexane (200 mL). The product was collected by filtration and dried under reduced pressure at 40 °C. The number averaged molecular weight (M_n = 14400) and the polydispersity index (PDI = 1.04) were determined by GPC calibrated with poly(methyl methacrylate) standards.

Correlation of M_n and amount of *N*-isopropylacrylamide used of each experiments using **1a** by changing *N*-isopropylacrylamide/**1a** ratio are shown (Figure S5).

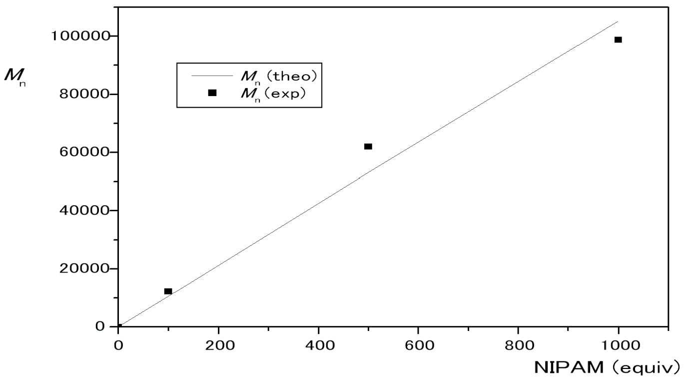


Figure S5. Correlation of experimental and theoretical molecular weight (M_n) of poly(*N*-isopropylacrylamide) in the bulk polymerization of *N*-isopropylacrylamide with **1a** as a function of the amount of *N*-isopropylacrylamide used (100 – 1000 equiv).

Typical procedure of polymerization of *N*-vinylpyrrolidinone. A solution of *N*-vinylpyrrolidinone (1.11 g, 10 mmol), mediator **1a** (41 μL, 0.1 mmol), and AIBN (3.3 mg, 0.02 mmol) was heated at 60 °C for 3 h with stirring under nitrogen atmosphere in a glove box. A small portion of the reaction mixture was withdrawn and dissolved in $CDCl_3$. The conversion of monomer (94%) was determined by ^{1}H NMR. The rest of reaction mixture was dissolved in $CHCl_3$ (4 mL) and poured into a vigorously stirred hexane (200 mL). The product was collected by filtration and dried under reduced pressure at 40 °C. The number averaged molecular weight (M_n = 11,100) and the polydispersity index (PDI = 1.06) were determined by GPC calibrated with poly(methyl methacrylate) standards.

Correlation of M_n and amount of *N*- vinylpyrrolidinone used of each experiments using **1a** by changing *N*- vinylpyrrolidinone/**1a** ratio are shown (Figure S6).

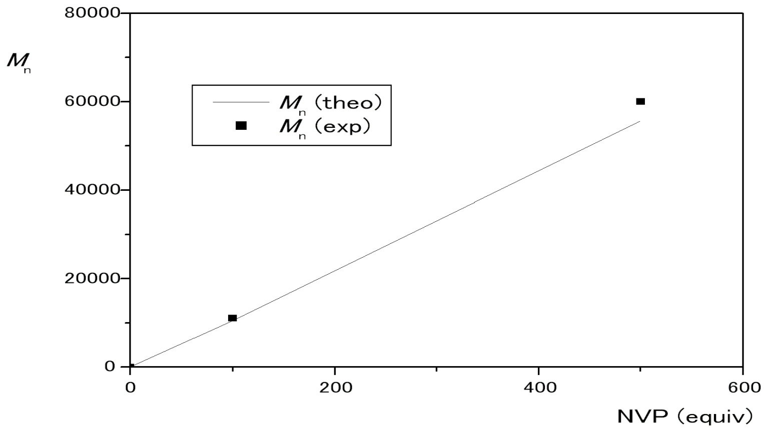


Figure S6. Correlation of experimental and theoretical molecular weight (M_n) of poly(*N*-vinylpyrrolidinone) in the bulk polymerization of *N*-vinylpyrrolidinone with **1a** as a function of the amount of *N*-vinylpyrrolidinone used (100 – 500 equiv).

Preparation of polystyrene-macromadiator. A mixture of mediator **1a** (38 µL, 0.2 mmol) and styrene (0.57 mL, 5 mmol) was heated to 100 ºC for 3 h with stirring under nitrogen atmosphere in a grove box. A small portion of the reaction mixture was withdrawn and dissolved in $CDCl_3$. The conversion of monomer (94%) was determined by ^1H NMR. The rest of reaction mixture was dissolved in $CHCl_3$ (4 mL) and poured into a vigorously stirred methanol (200 mL) under nitrogen atmosphere in a glove box. The product was collected by filtration in the glove box and dried under reduced pressure at room temperature. The number averaged molecular weight (M_n = 6000) and the polydispersity index (PDI = 1.07) were determined by GPC calibrated with polystyrene standard.

Synthesis of PSt-*b*-PVP block copolymer. A mixture of polystyrene macromediator (0.62 g, 0.1 mmol, M_n = 6000, PDI = 1.07), AIBN (3.3 mg, 0.02 mmol), and *N*-vinylpyrrolidone (1.06 mL, 10 mmol) in DMF (1.0 mL) was heated to 60 °C for 16 h with stirring under nitrogen atmosphere in a glove box. A small portion of the reaction mixture was withdrawn and dissolved in $CDCl_3$. The conversion of monomer (93%) was determined by ^1H NMR. The rest of mixture dissolved in $CHCl_3$ and was poured into a vigorously stirred hexane (200 mL). The product was collected by filtration and dried under reduced pressure at 40 °C. The number averaged molecular weight (M_n = 15100) and the polydispersity index (PDI = 1,16) were determined by GPC calibrated with poly(methyl methacrylate) standards (Figure S7).

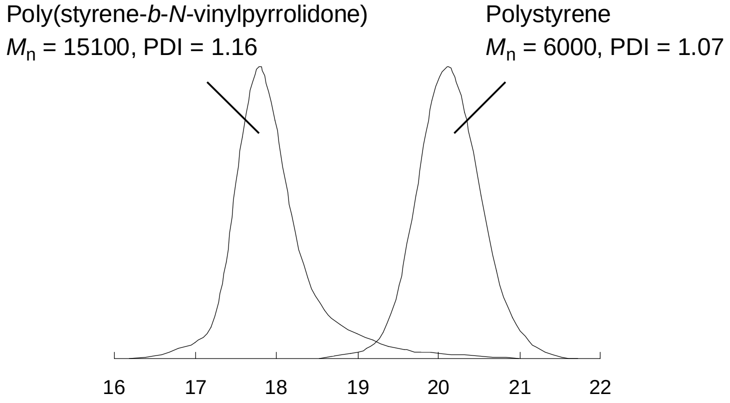


Figure S7. GPC traces of starting polystyrene macromediator and the resulting diblock copolymer

Experimental procedure for determining k_{ex} and k_d. A PSt-dimethylbismuthine adduct **3** (M_n = 2900, PDI = 1.10) was obtained as described above. This polymer was used as a probe adduct (P_0-X) (see below). A chain extension test[3] showed that this polymer contains 3 % of inactive species without the dimethylbismuthine group at the chain end. The experimental data presented below (Figure S8) have been corrected for this impurity.[4,5] A Schlenk flask was charged with a St solution (3 mL) of P_0-X (3.0 mM) and 2,2-Azobis(2,4,4-trimethylpentane) (VR-110) (0-36 mM) in a glove box under argon atmosphere, equipped with a stopcock, and immersed in an oil bath at 100 °C with magnetic stirring (t = 0). After a prescribed time t, an aliquot (0.1 mL) of the solution was taken out with a syringe, quenched in the air at room temperature, diluted by THF to a known concentration, and analyzed by GPC.

Kinetic analysis for determining k_{ex} and k_d. BIRP possibly includes thermal dissociation (TD: Scheme S1) and degenerative chain transfer (DT: Scheme S1) as the activation processes. If both processes coexist, the pseudo-first-order activation rate constant k_{act} (Scheme S1) will take the form[3]

$$k_{act} = k_d + k_{ex}[P^\bullet] \qquad \text{(S1)}$$

in which k_d and k_{ex} are the rate constants for TD and DT, respectively (Scheme S1). Therefore, by determining k_{act} as a function of the polymerization rate R_p (hence $[P^\bullet]$), we can obtain k_d and k_{ex}.

We examined the polymerization of St with a fixed amount of P_0-X (3.0 mM) and various amounts of VR110 (0-36 mM) at 100 °C. In all cases, the first-order plot of the monomer concentration [M] was linear, from the slope of which R_p was obtained. As expected, R_p increased with $[\mathrm{VR110}]_0$.

The k_{act} was determined by the GPC peak resolution method.[4] When P_0-X is activated, the released $P_0^\bullet$ will propagate until it is deactivated to give a new adduct P_1-X. (The subscripts 0 and 1 denote the number of activation.) Since P_0-X and P_1-X are generally different in chain length and its distribution, they may be distinguishable by GPC. By following the decay in $[P_0\text{-X}]$, k_{act} can be determined from the first-order plot

$$\ln(I_0/I) = k_{\mathrm{act}}t \tag{S2}$$

in which I_0 and I are the concentrations of P_0-X at times zero and t, respectively. A lower $[P_0\text{-X}]_0$ leads to a larger number of monomer units added to $P_0^\bullet$ during an activation-deactivation cycle.[6] In fact, with a sufficiently low $[P_0\text{-X}]_0$ (3.0 mM in this case), GPC chromatograms were composed of two peaks, allowing accurate resolution. The plot according to eq S2 was linear in all cases, from which k_{act} was obtained.

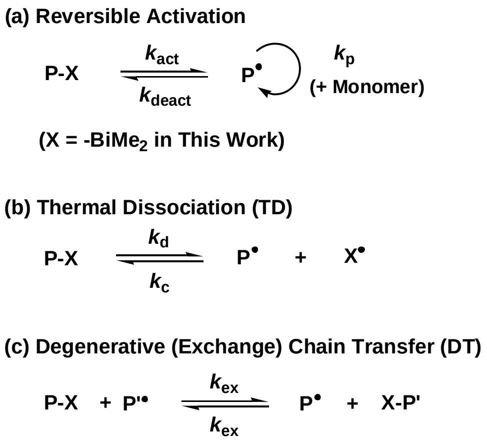
We alternatively determined k_{act} by the polydispersity analysis method.[5] We used the following relations that are valid for the "ideal" living radical polymerization in which reactions other than activation, deactivation, and propagation are absent, and $[P^\bullet]$ is constant.

$$Y = w_A^2 Y_A + w_B^2 Y_B \tag{S3}$$

$$F(c)[Y_B - (1/x_{n,B})]^{-1} = k_{act}t \tag{S4}$$

Here the product polymer at time t is viewed as an A-B block copolymer with the subchains A and B referring to P_0-X and the incremental part of the molecule, respectively; $Y = (x_w/x_n) - 1$, $Y_K = (x_{w,K}/x_{n,K}) - 1$, $w_A = 1 - w_B = x_{n,A}/x_n$, $x_n = x_{n,A} + x_{n,B}$, and x_n and x_w are the number- and weight-average degrees of polymerization (K = A or B). The c is the conversion and $F(c) = (1-2c^{-1})\ln(1-c)$ for a batch polymerization. Since we can measure the overall degrees of polymerization (x_n and x_w) and those of the subchain A ($x_{n,A}$ and $x_{w,A}$), we can calculate $x_{n,B}$ and Y_B according to eq S3, and then determine k_{act} according to eq S4. Prerequisites for this method to be valid are the constancy of both $[P^\bullet]$ (hence $R_p/[M]$) and the number of polymer chains N_p. The concentration $[N_p]$ estimated by c and x_n exceeded in no case 5 % of $[P_0\text{-X}]_0$, which, along with the linear first-order plot of [M] mentioned above, confirms that the prerequisites were approximately met in this experiment. The plot according to eq S4 was almost linear in all cases, from which we obtained k_{act}.

Figure S1 shows the plot of k_{act} vs $R_p/[M]$ (= $k_p[P^\bullet]$) at 100 °C according to eq S1, where k_p is the propagation rate constant. The peak resolution (filled circle) and polydispersity analysis (open circle) methods gave almost identical k_{act}. The plot was linear, and from the intercept and slope of the line, we obtained $k_d = 3\times10^{-5}$ s^{-1} and the exchange constant C_{ex} (= k_{ex}/k_p) = 40, respectively. With the known k_p (= 1100 M^{-1} s^{-1}), k_{ex} was calculated to be 4.6×10^5 M^{-1} s^{-1}.



Scheme S1. Reversible Activation Processes in Living Radical Polymerization (X = -BiMe$_2$ in This Work).

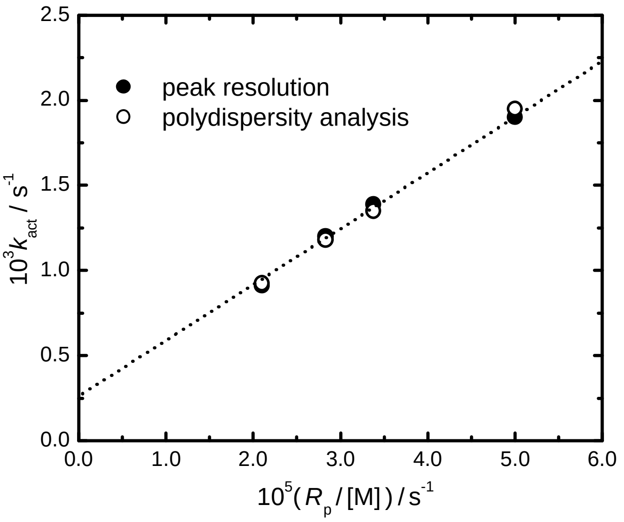


Figure S8. Plot of k_{act} vs (R_p/[M]) for the St/PSt-BiMe$_2$(P$_0$-X)/VR110 system at 100 °C: [P$_0$-X]$_0$ = 3.0 mM; [VR110]$_0$ = 0-36 mM. The k_{act} was determined by the GPC peak resolution (?) and polydispersity analysis (?) methods.

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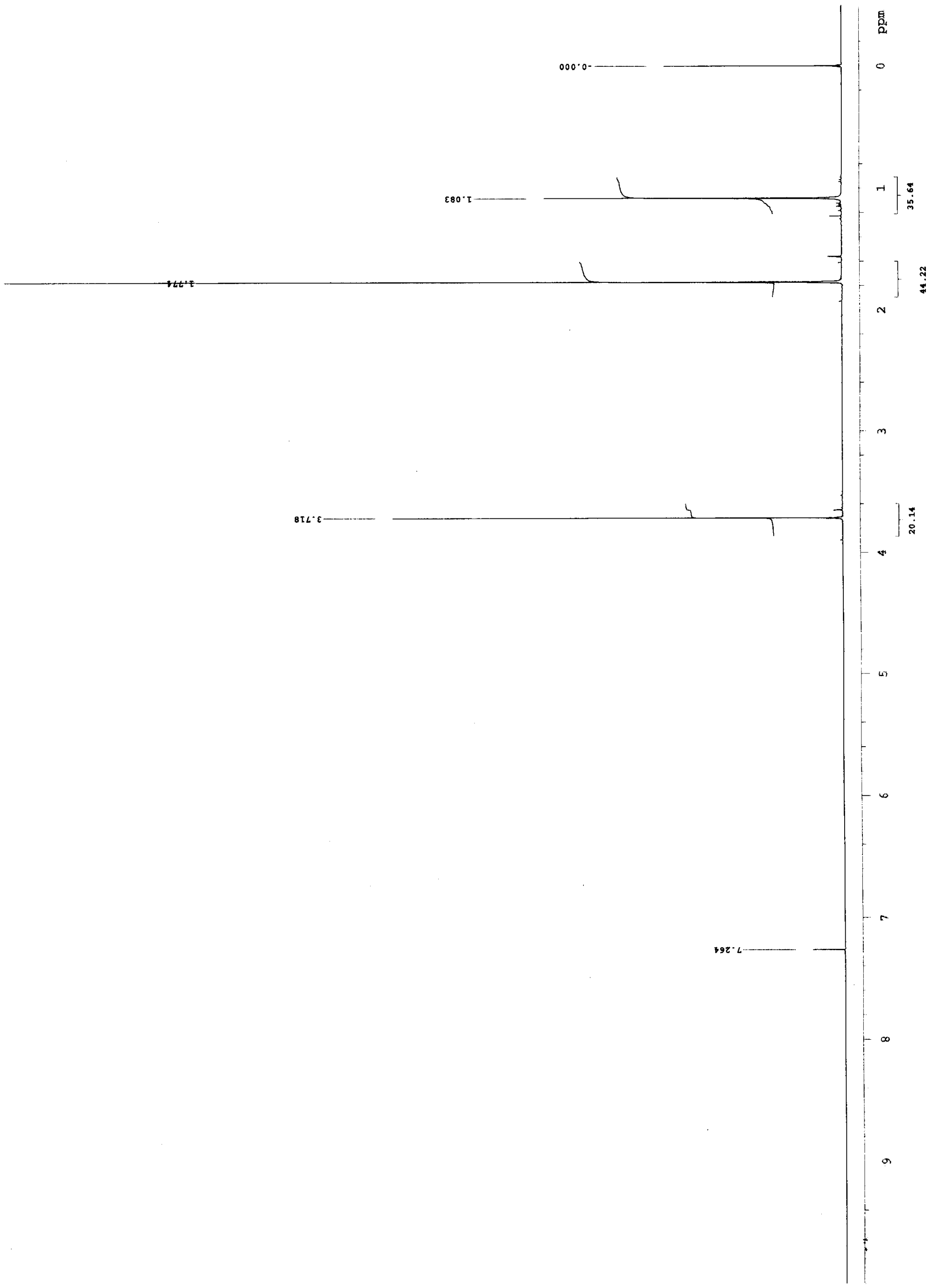
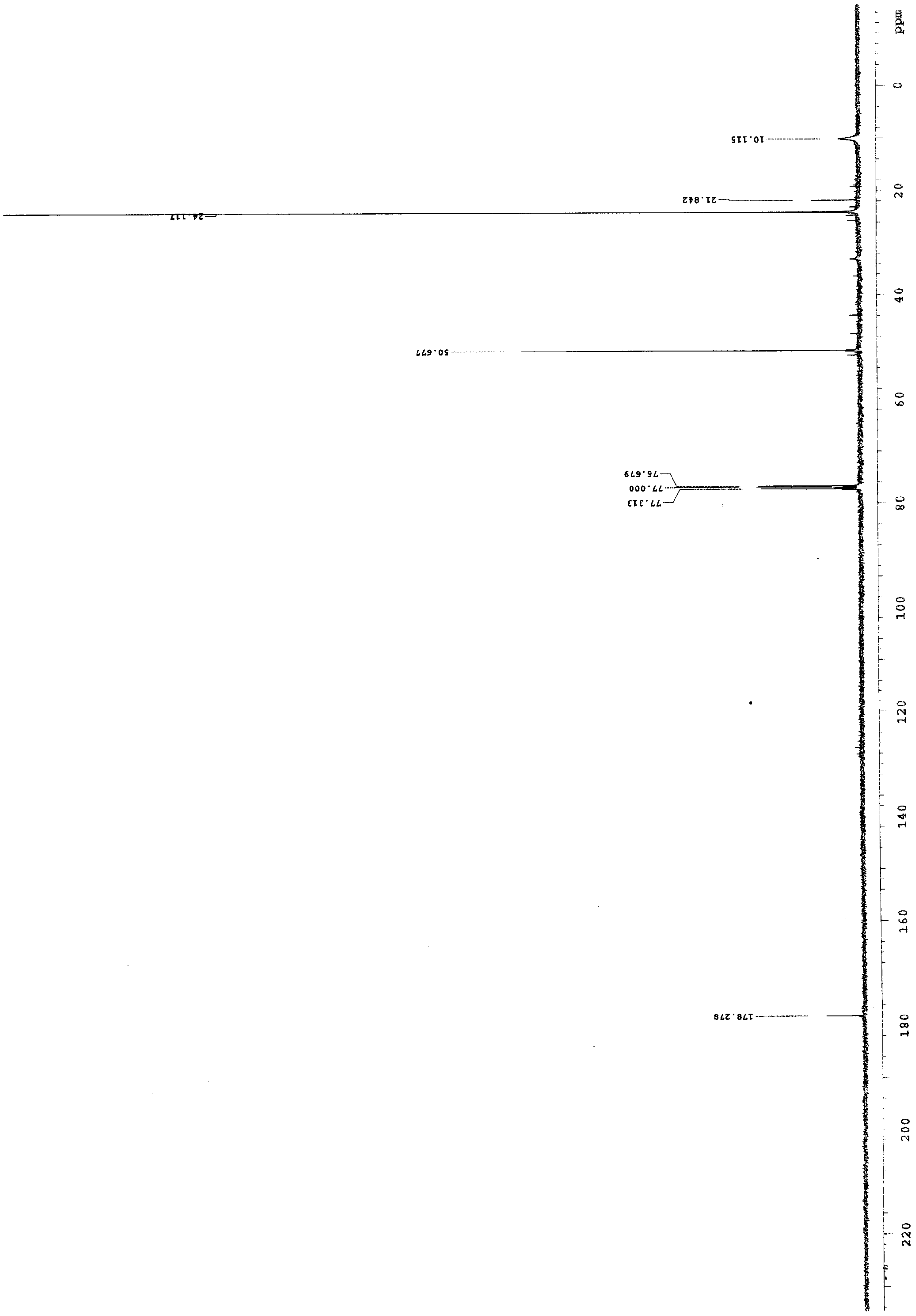
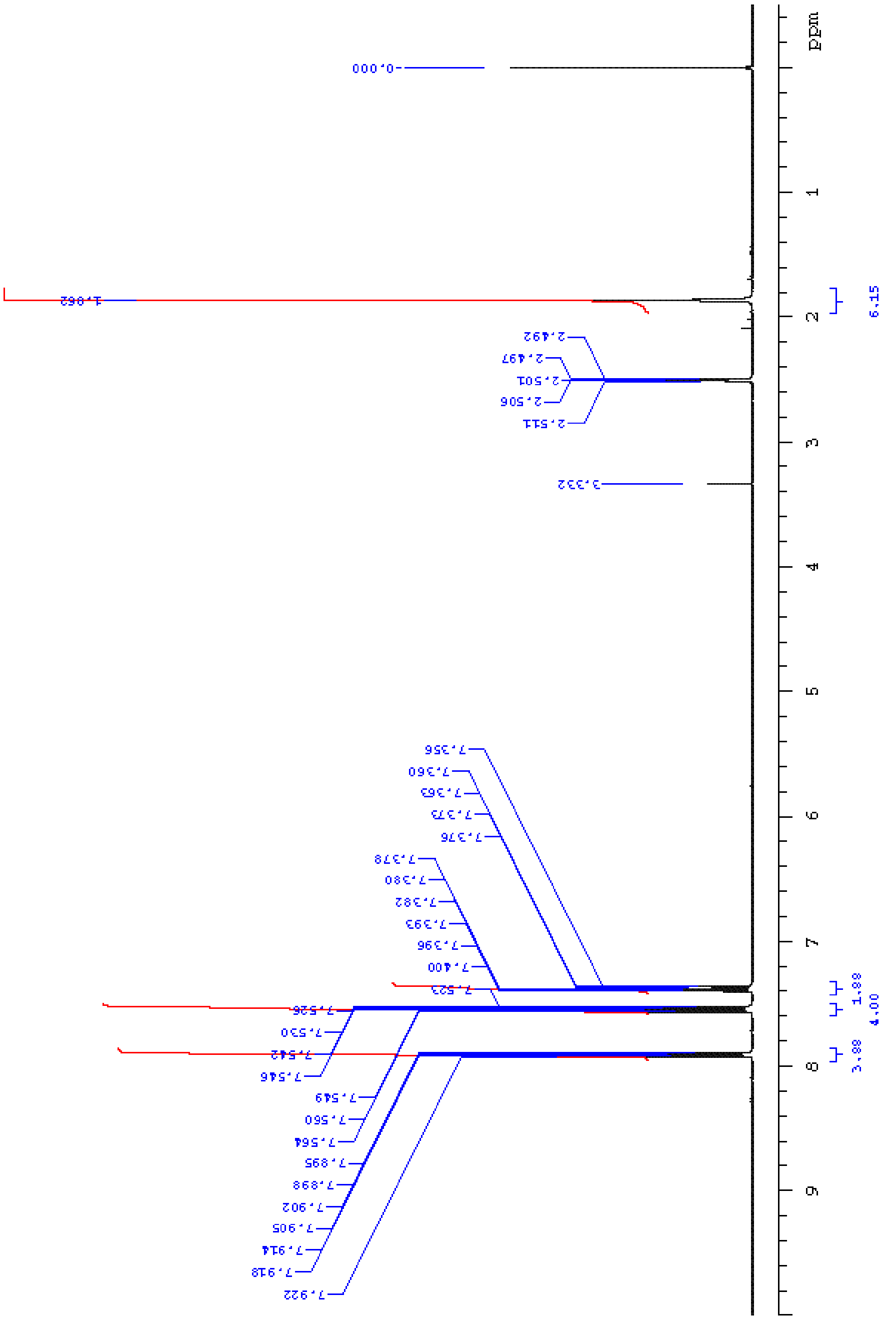
^{1}H NMR of **1a** in CDCl$_3$.



^{13}C NMR of **1a** in $CDCl_3$.



^{1}H NMR of **1b** in DMSO-d$_6$.



^{13}C NMR of **1b** in DMSO-d_6.