# Highly Controlled Synthesis of Poly(*N*-vinylpyrrolidone) and Its Block Copolymers by Organostibine-Mediated Living Radical Polymerization

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ABSTRACT: Poly(*N*-vinylpyrrolidone)s (PNVPs) with well-defined macromolecular structure were prepared by organostibine-mediated living radical polymerization. PNVPs with expected number-average molecular weight ($M_n$ = 3000−84 000) and low polydispersity indexes (PDIs = 1.1−1.3) were formed by heating a solution of organostibine mediator and NVP in the presence of AIBN at 60 °C. The polymer structure was analyzed by matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass and $^2$H NMR spectroscopies after reduction of the organostibanyl polymer end by tributyltin deuteride. The analyses reveal that, while the addition of AIBN considerably enhances the rate of the polymerization, the effect of azobis(isobutyronitrile) (AIBN)-derived radical to the $\omega$-end structure is negligible. The analyses also reveal the existence of "dead" dormant species due to head-to-head addition followed by the organostibanyl group transfer. However, since the probability of the head-to-head addition is small (0.02−0.10%) compared to the normal head-to-tail addition, its effect on the controllability was negligible under the current conditions. Diblock copolymers poly(styrene [St]-*block*-NVP), poly(methyl methacrylate [MMA]-*block*-NVP), and poly(NVP-*block*-MMA) were successfully prepared by successive addition of corresponding monomers to the organostibine macromediators.

## Introduction

Poly(*N*-vinylpyrrolidone) (PNVP) is a water-soluble and biocompatible polymer and has been extensively used in pharmaceuticals, cosmetics, foods, printing inks, textiles, and many more diverse applications.[1] Because of its versatilities, PNVP and its copolymers have also found numerous applications in modern biological and material sciences and technologies.[2] Therefore, control of macromolecular structure of PNVP and its copolymers would provide advanced materials with improved and/or new properties, but there are a few reports on the precise control of molecular structure of PNVP. Rimmer and Smith recently reported that PNVPs with low polydispersity index (PDI = $M_w/M_n$ < 1.5) could be synthesized upon employing 3-methylbutan-2-one as a chain transfer agent.[3] However, this method is limited to the synthesis of low molecular weight polymers (number-average molecular weight [$M_n$] < 10 000) due to termination of the polymer-end radicals with the chain transfer agent.

An alternative and more attractive strategy would be to use living radical polymerizations (LRPs), which are now widely used for the controlled polymerization of a variety of functionalized monomers.[4] Nitroxide-mediated living radical polymerization,[5] atom transfer radical polymerization (ATRP),[6] and degenerative transfer polymerization using thiocarbonyl compounds, such as reversible addition−fragmentation chain transfer radical polymerization[7] and macromolecular design via the interchange of xanthates,[8] are representative methods, and we have recently reported new degenerative transfer polymerization using organotellurium compounds.[9−11] However, despite the recent rapid development of LRPs, only a single example has been reported so far for the controlled oligomerization of NVP under copper-catalyzed ATRP conditions ($M_n$ = 2000, PDI = 1.15).[12−15] Indeed, monomers polymerized under controlled manner by the known LRP methods are limited to conjugated monomers, and their applications to unconjugated monomers, e.g., vinyl chloride,[16] vinyl acetate,[17,18] NVP, and α-olefins,[19] is of limited success. This is probably due to the high reactivities of polymer-end radicals of unconjugated monomers, which lack stabilizing groups and therefore tend to undergo several side reactions, such as disproportionation and chain transfer to form dead polymers. The high reactivity also corresponds to a higher rate constant for NVP polymerization than those of conjugated monomers. Therefore, it is also conceivable that inefficient deactivation would result in the loss of controllability in NVP polymerization because efficient deactivation of polymer-end radicals to dormant species is essential to achieve high control in LRP.[20]

We have recently reported that organostibines serve as excellent promoters for highly controlled living radical polymerization.[21−23] While investigating scope and limitations of the organostibine-mediated living radical polymerization (SBRP), we found that several organostibines can control the polymerization of NVP. We report here the first successful synthesis of PNVP of high molecular weight ($M_n$ > 10 000) and its block copolymers by the SBRP. Preliminary results have been already reported,[21] and we report here the full details of this study.

## Experimental Section

**Materials.** Unless otherwise noted, reagents from suppliers were used as received. NVP (>99%, Aldrich), styrene (St; 99%, Kishida Chemical), and methyl methacrylate (MMA; 99%, Wako Pure Chemical) were washed with 5% aqueous sodium hydroxide solution and were distilled over calcium hydride under reduced pressure. Azobis(isobutyronitrile) (AIBN; 98%, Wako Pure Chemical) was recrystallized from methanol.

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**General.** $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Varian MERCURYplus AS400 spectrometer at ambient temperature in $CDCl_3$ as solvent and are reported in parts per million ($\delta$) from internal tetramethylsilane or residual solvent peak. $^2$H NMR (92 MHz) spectra were recorded in $CHCl_3$ as solvent. Infrared spectra were recorded on Shimadzu FTIR-8200PC and are reported in $cm^{-1}$. High-resolution mass spectra (HRMS) were obtained on a JEOL AX500 spectrometer under electron impact ionization conditions. MALDI-TOF mass spectra were recorded on a Bruker Daltonics Microflex spectrometer equipped with a 337 nm $N_2$ laser in the reflection mode and at 20 kV acceleration voltage. Samples were prepared from a tetrahydrofuran (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 on a Shodex GPC-101 liquid chromatograph equipped with two linearly connected Shodex KF-804L polystyrene (PSt) mixed gel columns (300 × 8.0 mm; bead size = 7 $\mu$m, pore size = 20−200 Å). Analyses were made at 40 °C in 0.01 mol $L^{-1}$ lithium bromide solution of *N*,*N*-dimethylformamide (DMF) with a flow rate of 1.0 mL/min with a refractive index (RI) detector using poly(methyl methacrylate) (PMMA) or polystyrene (PSt) standard samples. Preparative GPC was performed on a Japan Analytical Industry LC-928R equipped with two linearly connected GPC columns (JAIGEL 1H and 2H) using $CHCl_3$ as eluant.

**Preparation of Ethyl 2-Dimethylstibanyl-2-methylpropionate (1).** Lithium diisopropylamide (16.5 mL, 2.0 M solution in heptane/THF/ethylbenzene, 33 mmol) was slowly added to a solution of isobutyric acid ethyl ester (3.48 g, 30 mmol) in THF (50 mL) over 10 min at − 78 °C, and the resulting solution was stirred at this temperature for 1 h. Dimethylstibanyl bromide (6.9 g, 29.8 mmol)[24] was added, and the resulting solution was warmed to room temperature over 2 h. Solvent was removed under reduced pressure followed by distillation under vacuum to give the title compound as colorless liquid in 50% yield (bp 53−55 °C/1.6−1.8 mmHg; 3.98 g, 14.9 mmol). IR (neat): 2980, 2909, 2864, 1697, 1468, 1384, 1252, 1136, 1032, 770, 515. $^1$H NMR (400 MHz, $CDCl_3$): 0.76 (s, 6H), 1.26 (t, $J$ = 7.2 Hz, 3H), 1.43 (s, 6H), 4.11 (q, $J$ = 7.2 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): −1.51 ($CH_3$, 2C), 14.89 ($CH_3$), 23.59 ($CH_3$, 2C), 31.56 (C), 59.84 ($CH_2$), 176.67 (C=O). HRMS (CI) *m*/*z*: calcd for $C_8H_{18}O_2Sb$ $(M + H)^+$, 267.0345; found 267.0362.

**Preparation of 2-Dimethylstibanyl-2-methylpropionitrile (2).** Lithium diisopropylamide (16.5 mL, 2.0 M solution in heptane/THF/ethylbenzene, 33 mmol) was added to a solution of isobutyronitrile (2.07 g, 30 mmol) in THF (50 mL) over 15 min at − 78 °C, and the resulting mixture was stirred at this temperature for 1 h. Dimethylstibanyl bromide (3 mL, 6.95 g, 30 mmol) was added, and the resulting solution was warmed to room temperature over 2 h. Solvent was removed under reduced pressure followed by distillation under vacuum to give the title compound as white solid in 35% yield (bp 55−57 °C/ 3 mmHg; 2.3 g, 10 mmol); mp 56.0−58.0 °C. IR (Nujol): 2860, 2206, 1713, 1452, 1371, 1211, 1121, 1016, 933, 775, 721, 665, 517. $^1$H NMR (400 MHz, $CDCl_3$): 0.95 (s, 6H), 1.50 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): −0.43 ($CH_3$, 2C), 14.51 ($CH_3$, 2C), 25.22 (C), 126.11 (CN). HRMS (EI) *m*/*z*: calcd for $C_6H_{12}NSb$ $(M)^+$, 219.0008; found 219.0028.

**Preparation of Dimethyl(1-phenylethyl)stibane (3).** Small pieces of sodium (2.87 g, 125 mmol) was slowly added to a suspension of trimethylstibanyl dibromide (9.80 g, 30 mmol)[25] in liquid ammonia (ca. 100 mL) over 10 min at − 78 °C. The reaction mixture was stirred for 1 h at boiling point of liquid ammonia. Anhydrous ammonium bromide (2.94 g, 30 mmol) was slowly added, and the resulting mixture was stirred for 0.5 h. Liquid ammonia was removed by immersing the reaction vessel in a water bath, and THF (100 mL) was added to this mixture.[26] (1-Bromoethyl)benzene (6.11 g, 33 mmol) was added, and the resulting solution was stirred at room temperature for 4 h. Solvent was removed under reduced pressure followed by distillation under vacuum to give the title compound as colorless liquid in 43% yield (bp 53−57 °C/1.3 mmHg; 3.28 g, 12.8 mmol). IR (neat): 2980, 2903, 2864, 1599, 1491, 1450, 1375, 1202, 1013, 764, 698, 665, 515. $^1$H NMR (400 MHz, $CDCl_3$): 0.53 (s, 3 H), 0.63 (s, 3H), 1.60 (d, $J$ = 7.2 Hz, 3H), 2.99 (q, $J$ = 7.2 Hz, 1H), 7.02−7.06 (m, 3H), 7.21−7.25 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): −2.62 ($CH_3$), −2.09 ($CH_3$), 18.79 ($CH_3$), 29.78 (CH), 124.78 (CH), 126.45 (CH, 2C), 128.35 (CH, 2C), 146.51 (C). HRMS (EI) *m*/*z*: calcd for $C_{10}H_{15}Sb$ $(M)^+$, 256.0212; found 256.0207.

**Typical Experimental Procedure for the Polymerization of NVP.** A solution of organostibine **1** (26.7 mg, 0.10 mmol), AIBN (8.2 mg, 0.05 mmol), and NVP (1.11 g, 10 mmol) was heated at 60 °C for 0.5 h under a nitrogen atmosphere in a glovebox. A small portion (ca. 20 mg) of the reaction mixture was withdrawn and was dissolved in $CDCl_3$ (0.5 mL). Conversion of monomer (100%) was determined by $^1$H NMR by observing disappearance of vinylic signals at 4.3−4.4 ppm (2H) of NVP. The rest of the reaction mixture was dissolved in $CHCl_3$ (5 mL) and poured into vigorously stirred hexane (300 mL). The precipitated polymer was collected by suction and was dried under vacuum at 50 °C. Because of the difficulty to remove solvent completely as judged by $^1$H NMR, the yield obtained gravimetrically was slightly higher than 100%. Analytical GPC calibrated by PMMA standards indicated that the polymer formed with $M_n$ = 12 700 and PDI = 1.10.

**Deuterium Labeling of Polymer End.** A solution of organostibine **1** (80.1 mg, 0.30 mmol), AIBN (24.6 mg, 0.15 mmol), and NVP (1.00 g, 9 mmol) was heated at 60 °C for 1 h under a nitrogen atmosphere in a glovebox. Conversion of the monomer (95%) was determined by $^1$H NMR by calibrating integrated peak area of the residual vinylic signals at 4.3−4.4 ppm (2H) of the monomer and 3.0−3.4 ppm (2H) of the polymer. The resulting mixture was dissolved in 4 mL of trifluoromethylbenzene. Tributyltin deuteride (130.9 mg, 0.45 mmol) and AIBN (5.0 mg, 0.03 mmol) were added, and the resulting solution was heated at 80 °C for 1.5 h. The reaction mixture was poured into vigorously stirred hexane (200 mL), and the precipitated polymer was collected by suction and dried under vacuum at room temperature. Analytical GPC indicated that the polymer formed with $M_n$ = 2800 and PDI = 1.07. The polymer was further purified by preparative GPC (to remove residual organotin compounds) and analyzed by the MALDI-TOF mass spectrum (see Figure 6) and $^2$H NMR spectrum. $^2$H NMR ($CHCl_3$): 0.8 (br s), 1.2 (br s), 3.2 (br).

**Typical Synthetic Procedure for PSt Macromediator.** A solution of organostibine **1** (53.4 mg, 0.20 mmol) and styrene (1.04 g, 10 mmol) was stirred at 110 °C for 24 h under a nitrogen atmosphere in a glovebox. A small portion (ca. 20 mg) of the reaction mixture was withdrawn and was dissolved in $CDCl_3$ (0.5 mL). Conversion of monomer (96%) was determined by $^1$H NMR by calibrating integrated peak area of the residual vinylic signals at 5.2 ppm (1H) and 5.7 ppm (1H) of the monomer and 6.8−7.5 ppm of the monomer (6H) and the polymer (5H). The rest of the resulting mixture was dissolved in deaerated $CHCl_3$ (5 mL) and poured into vigorously stirred deaerated methanol (300 mL). The precipitated polymer was collected by suction and was dried under vacuum. The workup was also carried out under a nitrogen atmosphere in a glovebox. Analytical GPC calibrated by PSt standards indicated that the polymer formed with $M_n$ = 4100 and PDI = 1.04.

**Synthesis of PMMA Macromediator.** A solution of organostibine mediator **1** (106.8 mg, 0.40 mmol) and methyl methacrylate (2.00 g, 20 mmol) was stirred at 100 °C for 48 h under a nitrogen atmosphere in a glovebox. A small portion (ca. 20 mg) of the reaction mixture was withdrawn and was dissolved in $CDCl_3$ (0.5 mL). Conversion of monomer (80%) was determined by $^1$H NMR by calibrating integrated peak area of the residual methoxy signal at 3.8 ppm (3H) of the monomer and 3.6 ppm (3H) of the polymer. The rest of the resulting mixture was dissolved in deaerated $CHCl_3$ (5 mL) and poured into vigorously stirred deaerated hexane (300 mL). The precipitated polymer was collected by suction and was dried under vacuum at room temperature. The workup was also carried out under a nitrogen atmosphere in a glovebox. Analytical GPC calibrated by PMMA standards indicated that the polymer formed with $M_n$ = 4700 and PDI = 1.27.

**Table 1. Living Radical Polymerization of *N*-Vinylpyrrolidone (NVP) with Organostibine Mediators and Azobis(isobutyronitrile) (AIBN)[a]**

| run | mediator | NVP (equiv) | AIBN (equiv) | conditions (°C/h) | conv[b] (%) | $M_n$[c] (theor) | $M_n$[d] (exp) | PDI[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 30 | 0.25 | 60/1 | 97 | 3 300 | 3 100 | 1.07 |
| 2 | **1** | 100 | 0.50 | 60/0.5 | 100 | 11 130 | 12 700 | 1.10 |
| 3 | **2** | 100 | 0.25 | 60/1.5 | 94 | 10 600 | 11 800 | 1.10 |
| 4 | **2** | 100 | 0.50 | 60/0.8 | 95 | 10 600 | 10 700 | 1.12 |
| 5 | **3** | 100 | 0.25 | 60/4 | 94 | 10 600 | 11 100 | 1.12 |
| 6 | **3** | 100 | 0.50 | 60/3 | 96 | 10 700 | 11 800 | 1.12 |
| 7 | **1** | 200 | 0.50 | 60/1 | 100 | 22 300 | 28 300 | 1.09 |
| 8 | **1** | 300 | 0.50 | 60/1.5 | 99 | 33 000 | 34 700 | 1.14 |
| 9 | **1** | 500 | 0.50 | 60/2 | 100 | 55 500 | 59 500 | 1.18 |
| 10 | **1** | 1000 | 0.50 | 60/2 | 93 | 103 200 | 83 500 | 1.29 |

[a] A mixture of mediator, AIBN, and NVP was heated under a nitrogen atmosphere. Molar concentrations of mediator and AIBN were $9.1 \times 10^{-2}$ and $4.6 \times 10^{-2}$ mol $L^{-1}$, respectively. [b] Monomer conversion determined by $^1H$ NMR. [c] The theoretical number-average molecular weight ($M_n$) calculated from monomer/mediator ratio and monomer conversion. [d] The experimental $M_n$ and polydispersity index (PDI) determined by size exclusion chromatography calibrated by poly(methyl methacrylate) standards using 0.01 M LiBr solution of *N*,*N*-dimethylformamide as an eluate.

**Typical Synthetic Procedure for PNVP Macromediator.** A solution of organostibine **1** (176.2 mg, 0.66 mmol), AIBN (27 mg, 0.165 mmol), and NVP (2.12 g, 20 mmol) was stirred at 60 °C for 1 h under a nitrogen atmosphere in a glovebox. A small portion (ca. 20 mg) of the reaction mixture was withdrawn and was dissolved in $CDCl_3$ (0.5 mL). Conversion of monomer (97%) was determined by $^1H$ NMR. The rest of the reaction mixture was dissolved in deaerated $CHCl_3$ (5 mL) and poured into vigorously stirred deaerated hexane (300 mL). The precipitated polymer was collected by suction and was dried under vacuum at room temperature. The workup was also carried out under a nitrogen atmosphere in a glovebox. Analytical GPC calibrated by PMMA standards indicated the polymer formed with $M_n = 2800$ and PDI = 1.06.

**Typical Synthetic Procedure for Poly(St-*b*-NVP).** A solution of PSt macromediator ($M_n = 4100$, PDI = 1.04, 0.23 g, 0.05 mmol), AIBN (2.3 mg, 0.014 mmol), and NVP (0.64 g, 5.7 mmol) in 1 mL of DMF were stirred at 60 °C for 8 h under a nitrogen atmosphere in a glovebox. A small portion (ca. 20 mg) of the reaction mixture was withdrawn and was dissolved in $CDCl_3$ (0.5 mL). Conversion of monomer (87%) was determined by $^1H$ NMR. The rest of the resulting mixture was dissolved in $CHCl_3$ (5 mL) and poured into vigorously stirred diethyl ether (300 mL). The precipitated polymer was collected by suction and was dried under vacuum at 50 °C. Analytical GPC calibrated by PSt standards indicated the polymer formed with $M_n = 27\,400$ and PDI = 1.05.

**Synthesis of Poly(MMA-*b*-NVP).** A solution of PMMA macromediator ($M_n = 4700$, PDI = 1.27, 0.19 g, 0.04 mmol), AIBN (1.8 mg, 0.011 mmol), and NVP (0.50 g, 4.4 mmol) in 1 mL of DMF were stirred at 60 °C for 8 h under a nitrogen atmosphere in a glovebox. A small portion (ca. 20 mg) of the reaction mixture was withdrawn and was dissolved in $CDCl_3$ (0.5 mL). Conversion of monomer (99%) was determined by $^1H$ NMR. The rest of the resulting mixture was dissolved in $CHCl_3$ (5 mL) and poured into vigorously stirred diethyl ether (300 mL). The precipitated polymer was collected by suction and was dried under vacuum at 50 °C. Analytical GPC calibrated by PMMA indicated the polymer formed with $M_n = 20\,500$ and PDI = 1.31.

**Synthesis of Poly(NVP-*b*-MMA).** A solution of PNVP macromediator ($M_n = 3000$, PDI = 1.06, 0.14 g, 0.046 mmol), AIBN (1.9 mg, 0.012 mmol), and MMA (0.46 g, 4.6 mmol) in 1 mL of DMF was stirred at 60 °C for 8 h under a nitrogen atmosphere in a glovebox. A small portion (ca. 20 mg) of the reaction mixture was withdrawn and was dissolved in $CDCl_3$ (0.5 mL). Conversion of monomer (88%) was determined by $^1H$ NMR. The rest of the resulting mixture was dissolved in $CHCl_3$ (5 mL) and poured into vigorously stirred diethyl ether (300 mL). The precipitated polymer was collected by suction and was dried under vacuum at 50 °C. Analytical GPC calibrated by PMMA standards indicated the polymer formed with $M_n = 20\,400$ and PDI = 1.18.

## Results and Discussion

**1. Homopolymerization.** Bulk polymerization of NVP (30−100 equiv) was initially examined with organostibine mediator **1** (Figure 1) at 100−110 °C for 20−60 h, but the progress of the polymerization was very slow, and it was difficult to obtain sufficient polymer (no data are shown). The slow polymerization rate would be attributed to low initiation efficiency of radical generation from the mediator,[11] and the effect of radical initiators was examined. Azo-initiators, e.g., AIBN, considerably increased the rate of the polymerization and high monomer conversion was achieved. Thus, the polymerization of NVP (30 equiv) completed within 1 h at 60 °C by the addition of 0.25 equiv of AIBN, and the desired well-defined PNVP was obtained in almost quantitative conversion (97%) with low polydispersity index (PDI = 1.07, Table 1, run 1). The polymerization with 100 equiv of NVP also completed within 0.5 h by the addition of 0.50 equiv of AIBN to give well-defined PNVP (PDI = 1.10, run 2). The addition of AIBN did not cause conventional free radical polymerization to occur.

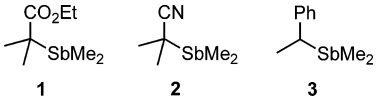



**Figure 1.** Chemical structure of organostibine mediators.

Organostibines **2** and **3** also promoted controlled polymerization of NVP in the presence of 0.25−0.50 equiv of AIBN at 60 °C, and PNVPs with predicted molecular weights and narrow molecular weight distributions were obtained in all cases (runs 3−6, PDI = 1.10−1.12). Organostibine **3** required longer reaction time for completion than **1** and **2**, and this can be attributed to the lower reactivity of the carbon-centered radical generated from **3** toward NVP than those from **1** and **2**. Despite the lower reactivity, **3** also promoted the controlled polymerization of NVP (runs 5 and 6).

High-molecular-weight polymers were obtained by increasing the amount of NVP toward the organostibine promoters (runs 7−10, Figure 2), and the results are consistent with the living character of the current polymerization. The experimentally obtained molecular weights slightly deviated from the linearity when 1000 equiv of NVP was employed, but PNVPs with unimodal and low polydisperisty indexes were obtained in all cases.

Living character of the current polymerization was confirmed by several control experiments. First, the molecular weight increased linearly with an increase in the amount of NVP used (Figure 2). Second, the number-average molecular weight also linearly increased with an increase of the conversion of NVP in experiment 1 with 300 equiv of NVP (Figure 3). The polydispersity index was high at low monomer conversion (PDI = 1.22 at 12% conversion), but it gradually decreased to 1.09 when about half amount of NVP was consumed. This behavior, namely decrease of polydispersity indexes with conversion of

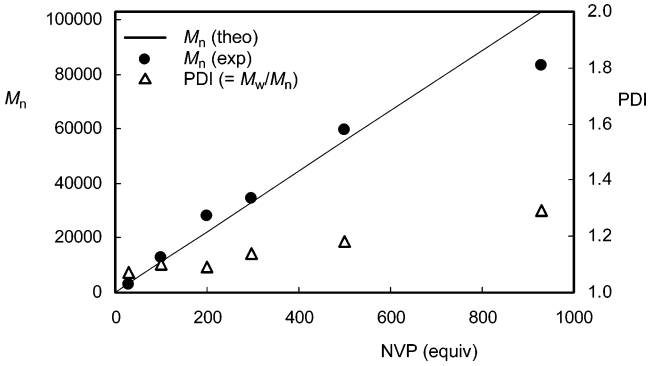



**Figure 2.** Correlation between number-average molecular weight ($M_n$; left ordinate) or polydispersity index (PDI; right ordinate) and equivalent of *N*-vinylpyrrolidone (NVP) in bulk polymerizations of NVP using organostibine mediator **1** and azobis(isobutyronitrile) at 60 °C.

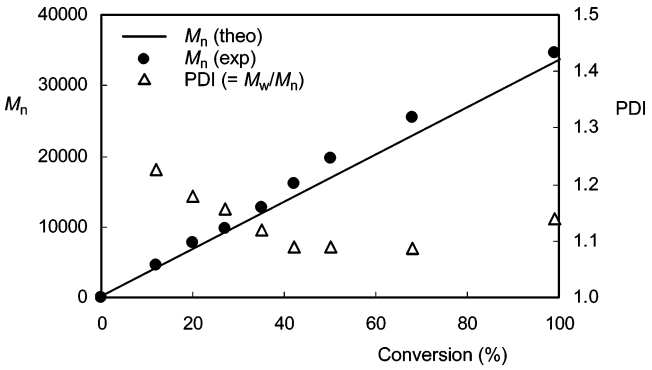



**Figure 3.** Correlation between number-average molecular weight ($M_n$; left ordinate) or polydispersity index (PDI; right ordinate) and conversion in a bulk polymerization of organostibine mediator **1** and 300 equiv of *N*-vinylpyrrolidone (NVP) in the presence of 0.50 equiv of azobis(butyronitrile) at 60 °C.

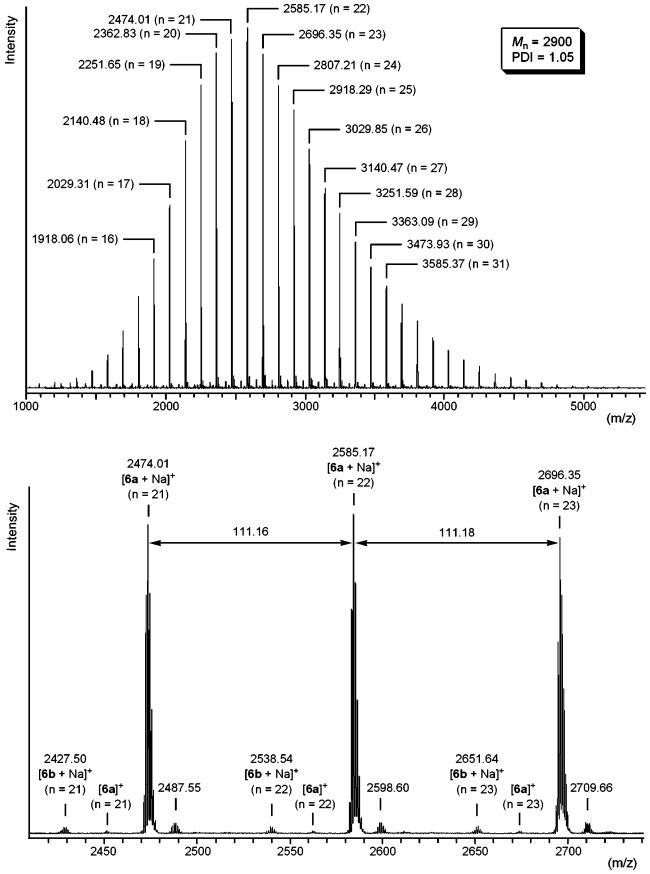
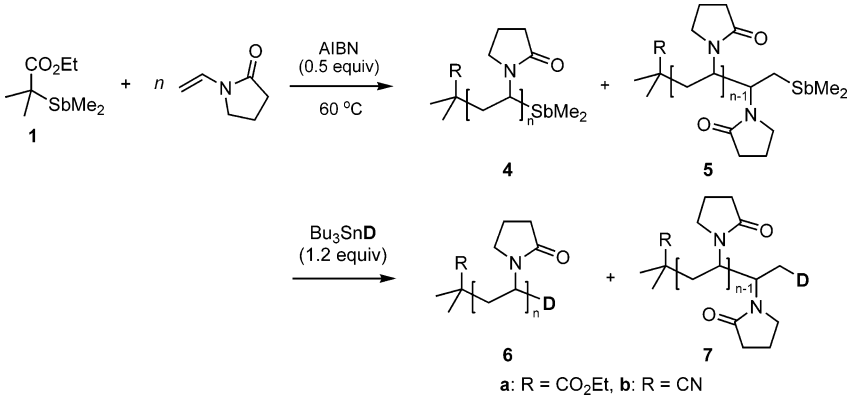



**Figure 4.** Full (top) and partial (bottom) mass spectra of end-deuterated poly(*N*-vinylpyrrolidone) (PNVP) obtained by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). A major series of peaks as indicated by average mass number are observed as sodium ion added form $(M + Na)^+$. Number-average molecular weight ($M_n$) and polydispersity index (PDI) shown here were obtained by the MS analysis.

the monomer, is also consistent with the livingness of the current polymerization.[20] However, after nearly 60% of monomer was consumed, PDI gradually increased and finally reached to 1.14 at 99% conversion. This unexpected result may be attributed to the formation of the head-to-head addition adduct to form the "dead" dormant species as discussed below.

**2. Analysis of Chain-End Structure.** Chain-end structure of the PNVP was further examined by deuterium labeling experiments. End-deuterated polymer was prepared with **1** and 30 equiv of NVP in the presence of 0.50 equiv of AIBN at 60 °C followed by tributyltin deuteride reduction of the dimethylstibanyl−polymer end (Scheme 1).[21] MALDI-TOF-MS analysis revealed the highly selective formation of a series of peaks (95%) corresponding to the molecular mass of **6a** as sodium ion attached forms (Figure 4). The MS spectra also indicate the formation of **6b** (3%), which was initiated by the AIBN-derived radical species, and 2% of uncharacterized polymer having 13−14 higher molecular mass than **6a**. The MS analysis clearly indicated the exclusive formation of polymers possessing organostibanyl end group, which was reduced to the corresponding deuterated end polymers by tributyltin deuteride. The analysis also revealed that, while the addition of AIBN considerably enhances the rate of the polymerization, the amount of polymers initiated from the AIBN-derived radical species (**6b**) is negligible (3%).

**Scheme 1. Synthesis of *ω*-End-Deuterated Poly(*N*-vinylpyrrolidone) (PNVP) by Organostibine 1 Mediated Polymerization of NVP in the Presence of Azobis(isobutyronitrile) (AIBN) Followed by Treatment of Tributyltin Deuteride**



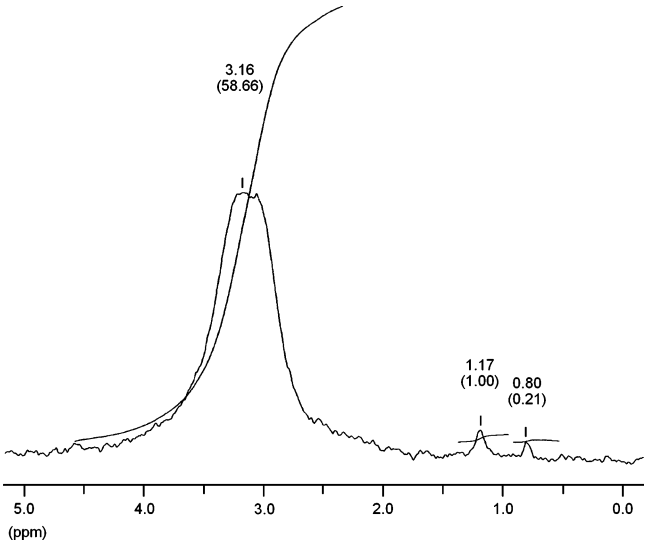



**Figure 5.** $^2$H NMR spectrum of end-deuterated poly(*N*-vinylpyrrolidone) (PNVP). Chemical shifts and integrated peak areas (in parentheses) are shown. The major peak at 3.16 ppm is assigned to the head-to-tail adduct **6**, and minor peaks at 1.17 and 0.80 ppm are assigned to the head-to-head adduct **7**.

**Table 2. Ratio of the Head-to-Head Addition in *N*-Vinylpyrrolidone (NVP) Polymerization**[a]

| run | NVP (equiv) | conv (%)[b] | $M_n$[c] | PDI[c] | **6**:**7**[d] | H−H (%)[e] |
|---|---|---|---|---|---|---|
| 1 | 30 | 95 | 3 200 | 1.08 | 98:2 | 0.08 |
| 2 | 200 | 94 | 22 500 | 1.12 | 92:8 | 0.04 |
| 3 | 500 | 88 | 65 300 | 1.16 | 90:10 | 0.02 |

[a] See text for the details. [b] Monomer conversion determined by $^1$H NMR. [c] The number-average molecular weight ($M_n$) and polydispersity index (PDI) determined by size exclusion chromatography calibrated by poly(methyl methacrylate) standards. [d] Product ratio of head-to-tail and head-to-head adducts determined by $^2$H NMR. [e] Probability of the head-to-head addition assuming that the head-to-head product (**5**) does not regenerate polymer-end radical.

The $^2$H NMR analysis of the deuterated polymer in $CHCl_3$, however, indicated the existence of structural isomers, which showed broad deuterium resonances at 3.2, 1.2, and 0.8 ppm as a 98:1.7:0.3 mixtures (Figure 5). The $^2$H NMR result is in sharp contrast to the similar analysis with polystyrene prepared from **1** and styrene,[9] in which only a single resonance derived from benzilic deuterium was observed. The deuterium chemical shifts of the polymer are similar to the ethyl group of *N*-ethylpyrollidone (3.33 and 1.12 ppm for α- and $\beta$-protons in $CDCl_3$, respectively). Therefore, the major resonance at 3.2 ppm was assigned as **6** and minor two resonances at 1.2 and 0.8 ppm as **7**; the former derived from polymer **4** formed by the head-to-tail addition followed by the dimethylstibanyl group transfer and the latter from **5** formed by the head-to-head addition (Table 2, run 1).

The formation of **7** was also observed in the deuterium labeling experiments in the experiments using 200 and 500 equiv of NVP (Table 2, runs 2 and 3). The ratio of **7** increases as the increase of the amount of NVP, and the results clearly indicate that the head-to-head adduct **5** accumulated in the reaction mixture as the degree of the polymerization increased. This is because regeneration of the primary radical from **5** is less favorable than the α-amino radical from **4** by considering the stability of the radical species. The formation of such head-to-head addition adduct has been reported in conventional and controlled radical polymerization of unconjugated monomers, e.g., vinyl acetate[17,27−29] and fluorinated monomers,[30] but this is the first example, as far as we know, to determine the existence of the head-to-head addition in the NVP polymerization.

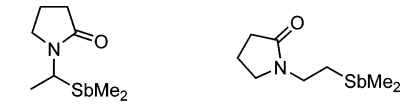



**Figure 6.** Carbon−antimony bond dissociation energies of polymer-end models obtained by the density functional theory (DFT) calculations at the B3LYP/6-31G* + LANL2DZ(Sb) level of theory.

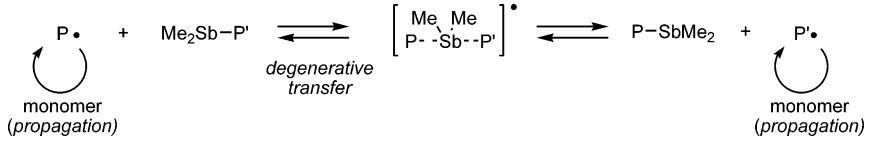
The density functional theory (DFT) calculations of polymer-end models revealed that the bond dissociation energies of **8** and **9** are 143 and 188 kJ/mol at the B3LYP/6-31G*+LANL2DZ-(Sb) level of theory, respectively (Figure 6). Since the bond dissociation energies are parallel to the stabilities of radical species, the calculation clearly suggested that polymer **5** is virtually inert toward radical generation under the present experimental conditions. Therefore, while both **4** and **5** possess dimethylstibanyl polymer ends, the latter behaves as dead polymer and is gradually accumulated in the reaction mixture as the degree of the polymerization increased.[29] The probability of the head-to-head addition could be calculated as 0.02−0.08% under an assumption that **5** is completely inert under the reaction conditions, and this value is considerably lower than that in vinyl acetate polymerization (1−2%).[18,28]

SBRP proceeds via degenerative transfer mechanism, in which polymer-end radical (P$^\bullet$) reacts with dormant organostibine compound (P′$SbMe_2$) to generate new dormant species ($PSbMe_2$) and P′ radical (Scheme 2).[21−23] The rate of the transfer should be sufficiently fast compared to the rate of propagation to obtain polymers with narrow molecular weight distributions.[20] Low polydispersity indexes observed in the current PNVP synthesis, especially in the synthesis of low-molecular weight PNVPs, strongly suggests that the rate of the degenerative transfer of dormant polymer **4** is sufficiently fast. In contrast, the transfer of the polymer-end radical with head-to-head adduct **5** does not occur efficiently. Since **5** is gradually accumulated in the reaction mixture as the progress of the poymerization, the polydispersity indexes gradually increase as the increase of the amount of NVP (Figure 2) and also as the increase of the conversion (Figure 3). A similar tendency, namely the increase of the polydispersity indexes as the increase of the degree of polymerization, has been also observed in vinyl acetate polymerization,[21] but the controllability of the resulting polymer is higher in the NVP polymerization than the vinyl acetate polymerization. This must be ascribed mainly to the low probability of the head-to-head addition in the NVP polymerization than vinyl acetate polymerization.[29]

**3. Block Copolymer Synthesis.** Synthesis of block copolymers possessing PNVP segment has been examined. While various block copolymers composed from conjugated monomers are synthesized by living radical polymerizations, controlled synthesis of block copolymers composed from conjugated monomers and nonconjugated monomers by successive addition of vinyl monomers has reported only recently.[14,21]

Since structure of mediator **3** is analogous to PSt polymer ends, synthesis of diblock copolymer composed of PSt and PNVP using PSt macromediator was initially examined. A PSt macromediator ($M_n$ = 4100, PDI = 1.04) was heated with NVP (100 equiv) and AIBN (0.25 equiv) in DMF (NVP:DMF = 1:2) at 60 °C for 8 h. GPC analysis of the resulting polymer revealed the disappearance of the PSt macropromoter and the formation of an unimodal polymer corresponding to poly(St-*b*-NVP) with

**Scheme 2. Degenerative Transfer Mechanism of Organostibine-Mediated Living Radical Polymerization (SBRP)[a]**




[a] The degenerative transfer takes place through tetravalent organostibine transition state or intermediate.

**Table 3. Synthesis of Block Copolymers[a]**

| run | macropromoter[b] ($M_n$/PDI)[d] | monomer[b] (equiv) | conditions (°C/h) | conv[c] (%) | $M_n$[d] | PDI[d] | $X_{monomer}$[e] |
|---|---|---|---|---|---|---|---|
| 1 | PSt (4100/1.04) | NVP (100) | 60/8 | 87 | 27 400 | 1.05 | 0.22 |
| 2 | PSt (24200/1.11) | NVP (200) | 60/24 | 77 | 50 900 | 1.27 | 0.36 |
| 3 | PSt (24200/1.11) | NVP (500) | 60/21 | 63 | 74 100 | 1.28 | 0.30 |
| 4 | PMMA (4700/1.27) | NVP (100) | 60/8 | 99 | 20 500 | 1.31 | 0.22 |
| 5 | PNVP (2800/1.06) | St (100) | 60/8 | 14 | 11 900 | 1.12 | 0.38 |
| 6 | PNVP (3000/1.06) | MMA (100) | 60/8 | 88 | 20 400 | 1.18 | 0.18 |

[a] A mixture of macropromoter, AIBN (0.25 equiv), and monomer in DMF was heated under a nitrogen atmosphere. [b] (P)St: (poly)styrene, (P)MMA: (poly)methyl methacrylate, (P)NVP: (poly)*N*-vinylpyrrolidone. [c] Monomer conversion determined by $^1$H NMR. [d] The number-average molecular weight ($M_n$) and polydispersity index (PDI) determined by size exclusion chromatography calibrated by PMMA standards for runs 4 and 6 and PSt standards for others using 0.01 mol L$^{-1}$ LiBr solution of *N*,*N*-dimethylformamide as an eluate. [e] Mole fraction of the first monomer determined by $^1$H NMR in $CDCl_3$ at room temperature.

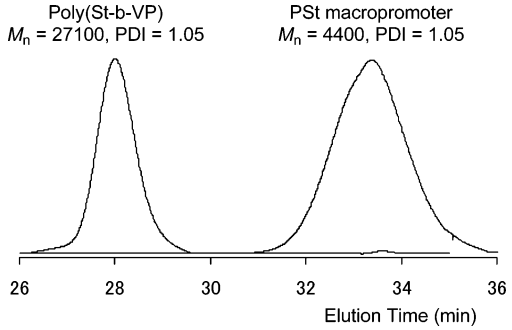



**Figure 7.** Gel permeation chromatography (GPC) traces of polystyrene (PSt) macropromoter and resulting poly(styrene [St]-*b*-*N*-vinylpyrrolidone [NVP]) after treatment of the macropromoter with 100 equiv of NVP and 0.25 equiv of azobis(isobutyronitrile) in *N*,*N*-dimethylformamide at 60 °C for 8 h.

$M_n$ = 27 400 and PDI = 1.05 in 87% yield (Table 3, run 1 and Figure 7). The GPC trace clearly revealed that activation of PSt polymer end occurred efficiently under the reaction conditions. By altering the molecular weight of PSt macropromoters and the amount of NVP, poly(St-*b*-NVP)s composed of different composition of PSt and PNVP segments were successfully synthesized under controlled manner (runs 2 and 3). Since these copolymers consist of nonpolar PSt segment and polar PNVP segment, their physical properties would be of great interest.

As an analogy of the successful polymerization of NVP using promoter **1**, synthesis of block copolymer starting from PMMA macromediator was examined. The polymerization was carried out using a PMMA macropromoter ($M_n$ = 4700, PDI = 1.27) with NVP (100 equiv) in the presence of AIBN (0.25 equiv) in DMF at 60 °C. While the consumption of the macromediator was observed, the resulting block copolymer possessed tailing in the low-molecular-weight region and a small shoulder in the high-molecular-weight region (Figure 8). The tailing may be attributed to the fast propagation of the NVP polymerization compared to the initiation of the PMMA macropromoter. Nevertheless, poly(MMA-*b*-NVP) with considerably controlled structure ($M_n$ = 20 500, PDI = 1.31) was obtained in quantitative yield (run 4).

Since the order of monomer addition is important in block copolymer synthesis, synthesis of same diblock copolymers by changing the sequences using a PNVP macromediator has been examined. While the chain extension from a PNVP macromediator to styrene was inefficient, that to MMA (100 equiv)

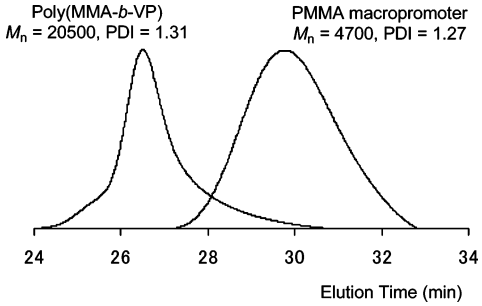



**Figure 8.** Gel permeation chromatography (GPC) traces of poly(methyl methacrylate) (PMMA) macropromoter and resulting poly(MMA-*b*-*N*-vinylpyrrolidone [NVP]) after treatment of the macropromoter with 100 equiv of NVP and 0.25 equiv of azobis(butyronitrile) in *N*,*N*-dimethylformamide at 60 °C for 8 h.

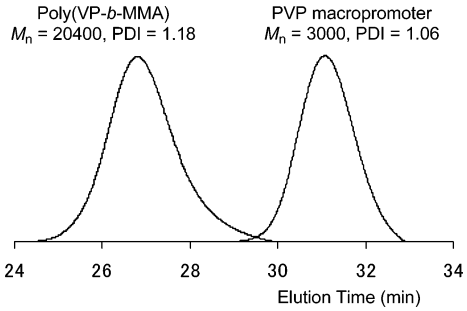



**Figure 9.** GPC traces of poly(*N*-vinylpyrrolidone) (PNVP) macropromoter and resulting poly(NVP-*b*-[methyl methacrylate] [MMA]) after treatment of the macropromoter with 100 equiv of MMA and 0.25 equiv of azobis(butyronitrile) at 60 °C for 8 h.

proceeded smoothly in the presence of AIBN to give highly controlled poly(NVP-*b*-MMA) with narrow molecular weight distribution (PDI = 1.18) (run 6). The GPC analyses indicated the clean conversion of the PNVP macromediator to the desired block copolymer (Figure 9).

## Conclusions

Organostibines are excellent mediators for the highly controlled living radical polymerization of NVP. Polydisperisty indexes of the obtained polymer are low (PDI ~ 1.1) when the targeted molecular weight is relatively low ($M_n$ < 15 000), but they slowly increase as the targeted molecular weight becomes higher. Deuterium-labeling experiments suggested that occurrence of the head-to-head addition is the major course of the

loss of the controllability upon the increase of the amount of NVP used. However, the probability of the head-to-head addition is so low that the level of the controllability was sufficiently high (PDI < 1.3) even in the high-molecular-weight PNVPs ($M_n \sim 100\,000$). A variety of diblock copolymers containing PNVP segment can be synthesized in a controlled manner. The mild reaction conditions and the high conversion make this process highly attractive to the practical synthesis of well structurally defined PNVP and its copolymers.

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