# Controlled Synthesis of Thiazole-Based Polymers and Block Copolymers by RAFT Polymerization of Azolyl S-Vinyl Sulfides and Metal Complexation

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**Supporting Information** 

**ABSTRACT:** We studied the RAFT polymerization of five *S*vinyl sulfide derivatives containing azole units, including 2benzothiazolyl vinyl sulfide (BTVS), 2-thiazolyl vinyl sulfide (2-TVS), 1,3,4-thiadiazolyl vinyl sulfide (1,3,4-TVS), 5-methyl-1,3,4-thiadiazolyl vinyl sulfide (M-1,3,4-TVS), and 5-phenyl-1,3,4-oxadiazolyl vinyl sulfide (P-1,3,4-OVS). The polymerization of BTVS using dithiocarbamate-type and trithiocar-



bonate-type chain transfer agents (CTAs) was controlled, as shown by the relatively low polydispersities of the polymers and the linear increase in molecular weight with increasing conversion. In addition, the molecular weight could be controlled by adjusting the monomer-to-CTA ratio. The thiazole-, thiadiazole-, and oxadiazole-based polymers with relatively narrow molecular weight distributions and predetermined molecular weights were obtained by RAFT polymerization of all monomers using the dithiocarbamate-type CTA. The formation of metal complexes between the azole-containing polymers and various metal species was investigated, concerning their optical and electrochemical behaviors, and the assembled structures of the metal—azole complexes. Among the combinations of the five polymers and three metal species (Cu, Zn, and Ni), the complexation between poly(BTVS) and copper species was the most strongly coordinating, affording a stable metal complex, poly(BTVS)-Cu. The fluorescence behavior of poly(BTVS)-Cu, which is induced by increasing the length of the conjugated structure between the benzothiazole rings and copper species, was controlled by the metal content in poly(BTVS)-Cu. The complexation of benzothiazole-based block copolymers, in which only the BTVS segment interacts with the copper species, whereas another styrene segment showed no specific interactions, exhibits characteristics of assembled structures and fluorescent properties.

# ■ INTRODUCTION

Azole compounds, such as imidazole, triazole, thiazole, and oxazole, are important and versatile five-membered nitrogen heterocyclic compounds containing at least one other noncarbon atom, that is, nitrogen, sulfur, or oxygen. A large number of azole-based derivatives have been developed, and these are used as antifungal drugs and agents, inhibiting fungal enzymes.<sup>1-3</sup> An attractive feature of azole compounds is that they bind easily with enzymes and receptors in organisms through noncovalent interactions such as hydrogen bonds, coordination bonds,  $\pi - \pi$  stacking, and van der Waals forces, which are often used in medical chemistry for drug design. Benzothiazole, which is a privileged heterocyclic compound that has a benzene ring fused to a thiazole ring, and its derivatives are common and integral features of a variety of natural products.<sup>5</sup> The benzothiazole unit has attracted a great deal of interest due to its wide range of pharmacological activities,<sup>5,6</sup> for example, its anticancer,<sup>7</sup> antitumor,<sup>8</sup> antimicrobial,<sup>9</sup> and antiallergic activities.<sup>10</sup> In addition to the wide variety of medical and biological applications, much attention has been paid to the complexation of azoles with various metal species.<sup>11-13</sup> For example, benzothiazole-derived Zn(II) complexes have been extensively studied, concerning their photophysical and electroluminescent properties, for applications in organic light-emitting diodes.<sup>14–16</sup> Metal complexes bearing pyridyl azolates, or a similar relevant functionality, have been developed as promising candidates for organic electronic and optoelectronic applications including organic light-emitting diodes and dye-sensitized solar cells.<sup>17</sup> Nitrogen-rich azolebased ligands have been employed as versatile building blocks for coordination-oligomer and polymer assemblies, including metal–organic frameworks.<sup>18</sup>

An intriguing feature of azole heterocycles is that the heteroatom participates in the  $\pi$  system, and this plays a crucial role in their characteristic optoelectronic properties. In particular, thiazole is a widely used electron-accepting heterocycle due to the electron-withdrawing nitrogen in the imine (C=N) function; consequently, various thiazole-based molecules have been introduced into organic semiconductors.<sup>19</sup> A wide variety of polymers containing thiazole, thiadiazole, and benzothiazole moieties in the side chains have been synthesized by conventional radical<sup>20–26</sup> and controlled radical polymerizations.<sup>27–33</sup> For example, Schubert et al. recently reported the controlled syntheses of methacrylate-based copolymers con-

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taining donor-acceptor thiazole dyes,<sup>27</sup> polystyrenes,<sup>28</sup> and polymethacrylates<sup>29</sup> containing thiazole-based, blue-emitting side-chains by reversible addition-fragmentation chain transfer (RAFT) polymerization. They also demonstrated the RAFT syntheses and investigated the energy transfer systems of polymethacrylates composed of thiazole-based chromophores and Os(II) metal complexes<sup>30</sup> and a statistical terpolymer containing a thiazole-based donor and an acceptor-type chromophore derived from Ru complex.<sup>31</sup> Atom transfer radical polymerization was also used for the production of well-defined polymethacrylates with pendant  $\pi$ -conjugated benzothiazole<sup>32</sup> and triblock copolymers composed of thiadiazole-containing oligoester.33 Conventional radical polymerizations of acrylamides containing benzothiazole units were used to develop fluorescent polymers involving an intra-molecular proton transfer.<sup>20,21</sup> Other examples involve the syntheses, by conventional radical polymerization, of antimicrobial polymethacrylates based on quaternized thiazole and triazole side-chain groups,<sup>22</sup> biologically active copolymers composed of thiazole-containing methacrylamide and oxazolecontaining methacrylate,<sup>23</sup> and an antimicrobial polymethacrylate with pendant thiadiazole units.<sup>24</sup> Because of scientific and industrial interest, several investigations have been made on thiazole-based polymer-metal complexes, which include thiazole-based polymethacrylamide-Cu(II) complexes having biological activity<sup>25</sup> and thiazole-based copolymer-metal (Ni<sup>2</sup> and Nd<sup>3+</sup>) complexes having characteristic magnetic properties.<sup>26</sup>

Oxadiazole-containing polymers have also attracted significant attention because oxadiazole compounds are electron deficient and have versatile electron transporting properties.<sup>34,35</sup> For example, random copolymers containing carbazole donor-oxadiazole acceptor side chains have been used as ambipolar hosts for phosphorescent light-emitting diodes<sup>36</sup> and for applications in high-performance-memory devices.<sup>37</sup> Similarly, RAFT polymerization of methacrylates containing holeor electron-transporting groups<sup>38</sup> and nitroxide-mediated radical polymerizations of styrene derivatives with hole/ electron transporting units<sup>39</sup> and luminescent/charge transport units<sup>40</sup> were used to synthesize oxadiazole-based polymers and diblock copolymers with well-defined structures. Conventional radical polymerization of oxadiazole-containing styrene derivatives resulted in the formation of a series of mesogen-jacketed liquid crystalline polymers.<sup>41</sup> Although these polymers containing thiazole, thiadiazole, and oxadiazole side chains have interesting properties, the monomers were limited to classical monomers, such as styrene, (meth)acrylate, and (meth)acrylamide derivatives.

Here, we present the controlled synthesis of azole-based polymers by RAFT polymerization of azolyl S-vinyl sulfides, including 2-benzothiazolyl vinyl sulfide (BTVS), 2-thiazolyl vinyl sulfide (2-TVS), 1,3,4-thiadiazolyl vinyl sulfide (1,3,4-TVS), 5-methyl-1,3,4-thiadiazolyl vinyl sulfide (M-1,3,4-TVS), and 5-phenyl-1,3,4-oxadiazolyl vinyl sulfide (P-1,3,4-OVS) (Scheme 1). Among them, BTVS and 2-TVS are thiazole derivatives, 1,3,4-TVS and M-1,3,4-TVS are categorized as thiadiazole derivatives, and P-1,3,4-OVS is an oxadiazole derivative. These azolyl S-vinyl sulfides have many attractive features, including an aromatic nucleus, high dipole moment, electron-accepting heterocycles, roles as ligands and coordination sites for metal species, and access to structurally diverse materials. Another attractive point is that the thioether group in the monomer unit can be readily converted to other functional





groups.<sup>42–44</sup> In addition, the binding of thioethers to transition metals, particularly concerning the coordination chemistry of Cu(II)-S species, has attracted significant interest because of their analogy to various class of metalloproteins, such as blue copper proteins.<sup>45–48</sup>

Recently, we investigated the controlled synthesis of sulfurcontaining polymers by RAFT polymerization of phenyl S-vinyl sulfide derivatives,  $^{49-52}$  which belong to a family of S-vinyl monomers. Generally, S-vinyl sulfides are donor monomers with  $\pi - \rho$  conjugation,<sup>53</sup> which are distinctly different form conventional styrene, (meth)acrylate, and (meth)acrylamidetype monomers. In the case of phenyl S-vinyl sulfide (Q = 0.32, e = -1.4), in which the sulfur atom is directly linked to the vinyl group, the 3d orbital resonance between the sulfur atom and the adjacent carbon atom is important in the copolymerization transition state formed with various comonomers. Similar to phenyl S-vinyl sulfide, in azolyl S-vinyl sulfides, a connection between the azole groups and the vinyl group through the thioether linkage, corresponding to  $\pi - \rho - \pi$ conjugation, exists. Consequently, the structure of the electron-accepting azole units in these monomers may affect the polymerization behavior, in addition to characteristic properties of the resulting S-vinyl heterocyclic polymers.

In this study, we initially investigated RAFT polymerization of five S-vinyl sulfide derivatives to afford well-defined poly(Svinyl sulfide)s with thiazole, thiadiazole, and oxadiazole side chains. Then, the formation of metal complexes between the azole-containing polymers with three metal species (Cu, Zn, and Ni) was investigated in terms of their optical and electrochemical behaviors and the structures of the metal complexes (Scheme 2). A key feature of this strategy is the

Scheme 2. Complexations of (a) Poly(BTVS) with Zn, Ni, and Cu Species and (b) Poly(S-vinyl sulfide) Derivatives with CuCl<sub>2</sub>



Poly(2-TVS) Poly(1,3,4-TVS) Poly(M-1,3,4-TVS) Poly(P-1,3,4-OVS)

CuCl <sub>2</sub>	Complexes			
DMF	with Cu			

incorporation of electron-deficient azole units into the *S*-vinyl monomers; this technique allows the controlled synthesis of azole-based polymers by RAFT polymerization and complexation with metal species. We also extended this methodology to develop novel metalloblock copolymers by the selective complexation of metal species with azole-based block copolymers. This is the first report on the controlled radical polymerization of azolyl *S*-vinyl sulfides, affording thiazole, thiadiazole, and oxadiazole-based homopolymers and block copolymers exhibiting characteristic complexation with metal species.

#### EXPERIMENTAL SECTION

**Materials.** 2,2'-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. Styrene (St, TCI, >99%) was purified by distillation under reduced pressure. Other materials were used without further purification.

Eight different chain transfer agents (CTAs) were employed in this study, as shown in Scheme 1. *O*-Ethyl-S-(1-ethoxycarbonyl)ethyl dithiocarbonate (CTA 1) and *O*-ethyl-S-(1-phenylethyl) dithiocarbonate (CTA 2)<sup>55,56</sup> were synthesized by the reaction of potassium ethyl xanthogenate with corresponding bromide (ethyl 2-bromopropionate for CTA 1 and 1-bromoethylbenzene for CTA 2) according to a procedure reported in the literature. Benzyl 1-pyrrolecarbodithioate (CTA 3),<sup>57,58</sup> benzyl dithiobenzoate (CTA 4),<sup>59,60</sup> and cumyl dithiobenzoate (CTA 5)<sup>61,62</sup> were synthesized according to the procedures reported previously. 2-Cyano-2-propyldodecyl trithiocarbonate (CTA 6, Aldrich, >97%), 4-cyano-4-[(dodecylsulfanyl-thiocarbonothioylthio)-2-methylpropanoic acid (CTA 8, Aldrich, >98%) were used as received.

Synthesis of Azolyl S-Vinyl Sulfides. Five azolyl S-vinyl sulfides, 2-benzothiazolyl vinyl sulfide (BTVS), 2-thiazolyl vinyl sulfide (2-TVS), 1,3,4-thiadiazolyl vinyl sulfide (1,3,4-TVS), 5-methyl-1,3,4thiadiazolyl vinyl sulfide (M-1,3,4-TVS), and 5-phenyl-1,3,4-oxadiazolyl vinyl sulfide (P-1,3,4-OVS) were synthesized by the reaction of 1,2-dibromoethane with the corresponding thiol compounds, according to a slightly modified reported method (Scheme S1, Supporting Information).<sup>49,63</sup> A typical experiment for the synthesis of BTVS is detailed here: 2-mercaptobenzothiazole (25.0 g, 0.15 mol) and 1,2-dibromoethane (56 g, 0.30 mol) were added to tetrahydrofuran (THF, 250 mL) at room temperature under a nitrogen atmosphere. To this mixture, 1,8-diazabicyclo[5.4.0]undec-7-ene (45 mL, 0.30 mol) was added dropwise with stirring at 0 °C. The reaction mixture was refluxed with stirring for 24 h, cooled, and treated with chloroform (300 mL) and water (300 mL). The organic layer was separated, washed with water, and dried over MgSO<sub>4</sub>. After filtration, the solvent was removed *in vacuo*, and the residue was distilled under reduced pressure to give pure BTVS as a pale yellow liquid (9.8 g, 34%).

BTVS: yield = 34%, bp 140 °C/0.05 mmHg (lit.<sup>64</sup> 163 °C/10 mmHg). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.0–7.2 (m, 4H, ArH), 7.1–7.0 (dd, 1H, CH<sub>2</sub>=CH–), 5.7 (dd, 2H, CH<sub>2</sub>=CH–) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  163.8 (SCS), 152.5 (NC), 133.4 (SC), 125.5, 123.7, 121.0, 120.2, 119.6 (CH<sub>2</sub>=CH–, ArC), ppm. Anal. Calcd for C<sub>9</sub>H<sub>7</sub>NS<sub>2</sub>: C, 55.92; H, 3.65; N, 7.25; S, 33.18. Found: C, 56.18; H, 3.75; N, 7.11; S, 32.87.

2-TVS: yield = 31%, bp 60 °C/0.05 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.7 (s, 1H, NCH=), 7.2 (s, 1H, SCH=), 6.8–6.7 (dd, 1H, CH<sub>2</sub>= CH–), 5.6–5.5 (dd, 2H, CH<sub>2</sub>=CH–) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 162.4 (SCS), 143.1 (NCH=), 128.1 (CH<sub>2</sub>=CH–), 119.8, 119.3 (SCH=, CH<sub>2</sub>=CH–) ppm. Anal. Calcd for C<sub>5</sub>H<sub>3</sub>NS<sub>2</sub>: C, 41.93; H, 3.52; N, 9.78; S, 44.77. Found: C, 42.01; H, 3.65; N, 9.56; S, 44.24.

1,3,4-TVS: yield = 21%; bp 100 °C at 0.05 mmHg. <sup>1</sup>H NMR (DMSO- $d_6$ ):  $\delta$  9.6 (s, 1H, SCH=N), 7.0–6.9 (dd, 1H, CH<sub>2</sub>=CH–), 5.9–5.8 (dd, 2H, CH<sub>2</sub>=CH–) ppm. <sup>13</sup>C NMR (DMSO- $d_6$ ):  $\delta$  163.6 (SCS), 154.8 (SCH=N), 126.9 (CH<sub>2</sub>=CH–), 121.4 (CH<sub>2</sub>=CH–) ppm.

M-1,3,4-TVS: yield = 20.9%, bp 130 °C/0.05 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.7 (dd, 1H, CH<sub>2</sub>=CH–), 5.5 (dd, 2H, CH<sub>2</sub>=CH–), 2.6 (s, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  160.4 (SCS), 162.6 (CH<sub>3</sub>C), 127.0 (CH<sub>2</sub>=CH–), 120.6 (CH<sub>2</sub>=CH–), 15.9 (CH<sub>3</sub>) ppm.

P-1,3,4-OVS: yield = 17.4%, bp 170 °C/0.05 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.0–7.7, 7.5 (m, 5H, ArH), 6.9–6.8 (dd, 1H, CH<sub>2</sub>=CH–), 5.7–5.6 (dd, 2H, CH<sub>2</sub>=CH–) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  165.9 (SCS), 162.0 (OCAr), 132.7, 128.9, 126.6, 123.8, 123.3, 121.0 (CH<sub>2</sub>=CH–, ArC) ppm. Anal. Calcd for C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>S<sub>2</sub>: C, 58.80; H, 3.95; N, 13.72; S, 15.70. Found: C, 59.15; H, 3.94; N, 13.86; S, 15.90.

<sup>1</sup>H and <sup>13</sup>C NMR spectra and the solubility of these monomers are shown in Figures S1 and S2 and Table S1, respectively (see Supporting Information). It was necessary to store the monomers under nitrogen in a freezer. In air at room temperature, pure BTVS existed as a pale yellow liquid was changed gradually into yellow liquid, whereas 1,3,4-TVS and M-1,3,4-TVS, which were transparent liquids initially, changed into dark red liquids after several weeks. The relative stabilities of these monomers were monitored by visual observation and decreased in stability in the following order: BTVS and P-1,3,4-OVS (more stable) > 2-TVS > 1,3,4-TVS and M-1,3,4-TVS (less stable).

General Polymerization Procedure. All polymerizations were carried out in a degassed sealed tube. A representative example is as follows: BTVS (0.39 g, 2.0 mmol), CTA 3 (4.7 mg, 0.02 mmol), and AIBN (1.6 mg, 0.01 mmol) were placed in a dry glass ampule equipped with a magnetic stirr bar, and then the solution was degassed by three freeze-evacuate-thaw cycles. After the ampule was flamesealed under vacuum, it was stirred at 70 °C for 24 h. Since the reaction was performed in bulk, the content of the flask was gradually changed from the light yellow liquid into viscous material with the polymerization time. The reaction was stopped by rapid cooling with liquid nitrogen. For the determination of the monomer conversion, the <sup>1</sup>H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in CDCl<sub>3</sub> at room temperature. The integration of the benzene ring protons of the side chain in polymer (4H) at 8.3–6.8 ppm was compared with the monomer  $CH_2$ =CHresonance (2H) at around 5.7 ppm. Conversion determined by this method was 60%. After the crude sample was dissolved in a small amount of chloroform, it was purified by reprecipitation into a large excess of methanol, and the resulting product was dried under vacuum at room temperature (0.176 g, 45%). The resulting poly(BTVS) was soluble in THF, 1,4-dioxane, chloroform, and DMF and insoluble in *n*-hexane, methanol, and water.

Similarly, poly(2-TVS), poly(1,3,4-TVS), poly(M-1,3,4-TVS), and poly(P-1,3,4-OVS) were prepared by RAFT polymerization of the corresponding S-vinyl sulfide derivatives (2-TVS, 1,3,4-TVS, M-1,3,4-TVS, and P-1,3,4-OVS). The <sup>1</sup>H NMR spectra and the solubilities of the resulting polymers are shown in Figures S3 and S4 and Table S1 (see Supporting Information).

The theoretical number-average molecular weight upon conversion is defined as follows:

$$M_{\rm n}({\rm theory}) = \frac{[{\rm Monomer}]_0}{[{\rm CTA}]_0} \times M_{\rm Monomer} \times {\rm conv} + M_{\rm CTA}$$
(1)

where  $M_{\text{CTA}}$  and  $M_{\text{Monomer}}$  are the molecular weights of CTA and monomer, and [Monomer]<sub>0</sub> and [CTA]<sub>0</sub> are the initial concentrations of monomer and CTA, respectively.

**Synthesis of Metal Complex.** The preparation of metal complexes was carried out according to an existing method.<sup>26</sup> The typical procedure is as follows; poly(BTVS) (0.10 g, 0.52 unit mmol based on the repeating unit) and  $CuCl_2$  (0.070g) (molar ratio of BTVS unit: $CuCl_2 = 1:1$ ) were dissolved in DMF at 5% concentration and stirred at 80 °C for 24 h under a nitrogen atmosphere. The final product was obtained by precipitating the resulting solution in methanol and filtering. The resulting product was dried under vacuum at 60 °C to yield poly(BTVS)-Cu as dark brown solid (0.073 g, 43%).

Synthesis of Block Copolymers. A representative example of the synthesis of the block copolymer composed of BTVS and St is as follows: BTVS (1.93 g, 10 mmol), CTA 6 (34.5 mg, 0.1 mmol), and AIBN (8 mg, 0.05 mmol) were placed in a dry ampule, and then the mixture was degassed by three freeze-evacuate-thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 6 h. After the product was purified by precipitation from a chloroform solution into a large excess of methanol, the product was dried under vacuum at room temperature to afford poly(BTVS) as a yellow solid  $(0.65 \text{ g}, 34\%, M_{\rm p} = 3500 \text{ g/mol}, M_{\rm w}/M_{\rm p} = 1.21)$ , which was employed as a macro-CTA. The trithiocarbonate-terminated poly(BTVS) (0.069 g, 0.02 mmol), AIBN (1.6 mg, 0.01 mmol), and St (0.208 g, 2.00 mmol) were placed in a dry ampule. After the solution was degassed by three freeze-evacuate-thaw cycles, the polymerization was conducted at 70 °C for 24 h. The reaction mixture was purified by reprecipitation from a chloroform solution into a large excess of hexane and isolated by filtration to give a block copolymer,

poly(BTVS)-*b*-poly(St), as a pale yellow solid. **Instrumentation.** <sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded with a JEOL JNM-ECX400. Elemental analysis was carried out on a PerkinElmer 2400 II CHNS/O analyzer. The number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) were estimated by size-exclusion chromatography (SEC) using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors at 40 °C. The column set was as follows: four consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs (bead size, exclusion limited molecular weight):  $\alpha$ -M (13 µm, >1 × 10<sup>7</sup>),  $\alpha$ -4000 (10 µm, 4 × 10<sup>5</sup>),  $\alpha$ -3000 (7 µm, 9 × 10<sup>4</sup>),  $\alpha$ -2500 (7 µm, 5 × 10<sup>3</sup>), 30 cm each] and a guard column [TSKguard column  $\alpha$ , 4.0 cm]. The system was operated at the flow rate of 1.0 mL/min using DMF containing 10 mM LiBr as the eluent. Polystyrene standards (Tosoh) ranging from 1050 to 1 090 000 were employed for calibration.

The UV-vis spectra were recorded using a JASCO V-630BIO UVvis spectrophotometer. The fluorescence spectra were obtained from a JASCO FP-6100 spectrofluorophotometer. Inductive-coupled plasma mass (ICP-MS) spectrometry measurements were performed on a PerkinElmer ELAN DRC II spectrometer. Nebulizer gas flow, ICP RF power, lens voltage, pulse stage voltage, dwell time, sweeps, readings per replicate, and flow rate were respectively as follows: 0.91-1.01 mL/min, 1.1 kW, 7.4 V, 900 V, 60 ns, 3 times, 3 times, and 0.96 mL/ min. Dynamic light scattering (DLS) was performed using a Zetasizer Nano (Sysmex) with a He–Ne laser. Thermogravimetric analysis (TGA) was performed on a SEIKO TGA/6200 at a heating rate of 10 °C/min under a nitrogen atmosphere. Cyclic voltammetry (CV) experiments were performed on a BAS electrochemical analyzer (model 660C) in the DMSO solutions with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte (scan rate: 0.1 V/s). A three-electrode cell was used with platinum electrodes as both the counter and working electrodes. Silver/silver ion (Ag in 0.1 M AgNO<sub>3</sub> solution) was used as the reference electrode. Ferrocene/ ferrocenium (Fc/Fc<sup>+</sup>) was used as an internal standard. The potential values obtained in reference to Ag/Ag<sup>+</sup> were converted to the values relative to the saturated calomel electrode (SCE).

# RESULTS AND DISCUSSION

Monomer Synthesis and Screening of Polymerization Conditions. Recently, we reported a series of investigations concerning the developments of vinyl heterocyclic compounds as building blocks for advanced functional materials, particularly N-vinyl<sup>65</sup> and S-vinyl<sup>49</sup> monomers applicable for controlled radical polymerizations. Key issues for further advances in this field include the development of effective synthetic methods, fine-tuning of the chemical structures of the heterocyclic compounds, their location and distribution, and manipulation of three-dimensional assembled structures under various environments. In this study, we synthesized a variety of Svinyl heterocyclic compounds, which were then used in RAFT polymerization to afford well-defined polymeric materials with various architectures and characteristic properties. Five S-vinyl sulfide derivatives having azole units (BTVS, 2-TVS, 1,3,4-TVS, M-1,3,4-TVS, and P-1,3,4-OVS, see Scheme 1) were synthesized by the reaction of 1,2-dibromoethane with corresponding thiol compounds. The synthesis was carried out following a previously reported, but slightly modified, method (Scheme S1, Supporting Information).<sup>49,63</sup> BTVS, 2-TVS, 1,3,4-TVS, and M-1,3,4-TVS are liquid at room temperature, whereas P-1,3,4-OVS was used as a solid monomer. This synthetic method is advantageous because it involves a simple one-step reaction and allows synthesis of structurally diverse polymers through the employment a variety of heterocyclic thiol compounds. Another attractive feature is their feasibility for use as azolebased heterocyclic building blocks and functional units for the construction of macromolecules, in which various properties can be manipulated by the structures of the heterocyclic units.

Initially, free radical polymerization of BTVS was investigated to find conditions for obtaining thiazole-based polymers having relatively high molecular weights with sufficient yields. Effects of the polymerization temperature and solvent on free radical polymerizations were examined with AIBN as an initiator at  $[M]_0/[I]_0 = 200$  under various conditions (see Tables S2, S3 and Figures S5, S6, Supporting Information). Bulk polymerization of BPVS at 70 °C afforded poly(BTVS) with reasonable monomer conversion (80%) and high molecular weights ( $M_n$  = 19 200,  $M_{\rm w}/M_{\rm n}$  = 1.97). Free radical polymerization of BTVS was also conducted at 100  $^\circ C$  using different initiators (Table S4). However, higher polymerization temperature led to the formation of the product having lower molecular weights, which could account for an inherent tendency to undergo chain transfer reactions at higher temperatures. We also investigated free radical polymerization of other azolyl S-vinyl sulfides (2-TVS, 1,3,4-TVS, M-1,3,4-TVS, and P-1,3,4-OVS; see Table S5 and Figure S7), indicating that similar polymerization behaviors were obtained, depending on the structure of the azole units. On the basis of these preliminary results, we selected bulk polymerization of BPVS at 70  $^{\circ}$ C for further investigations toward the synthesis of well-defined poly(azolyl S-vinyl sulfide)s.

RAFT Polymerization of 2-Benzothiazolyl Vinyl Sulfide (BTVS). The effect of the nature of the CTA on the radical polymerization of BTVS was investigated in the presence of AIBN as an initiator (Scheme 1). Previously, we reported that three mediating agents with different Z groups-O-ethyl-S-(1ethoxycarbonyl) ethyldithiocarbonate (CTA 1), benzyl 1pyrrolecarbodithioate (CTA 3), and 2-cyano-2-propyldodecyl trithiocarbonate (CTA 6)-were efficient to achieve controlled RAFT polymerization of phenyl S-vinyl sulfide derivatives,<sup>49–52</sup> in spite of the significant difference in the chain transfer constants. This may be due to the fact that S-vinyl sulfides have intermediate reactivity between the conjugated and nonconjugated monomers. On the basis of this, the bulk polymerization of BTVS was conducted with different CTAs at 70 °C for 24 h at  $[BTVS]_0/[CTA]_0/[AIBN]_0 = 200/2/1$ . The results are summarized in Table 1. Lowest polydispersities

Table 1. RAFT Polymerization of BTVS with AIBN Using Different CTAs in Bulk at 70 °C for 24  $h^a$ 

entry CTA (%) (theory) NMR) (SEC) (	· · ·
1 CTA 1 70 14000 $-^{e}$ 9400	1.57
2 CTA 2 70 14000 15000 10000	1.51
3 CTA 3 60 11000 14000 6100	1.18
4 CTA 4 40 8000 $-^{e}$ 1400	1.54
5 CTA 5 <5	-
6 CTA 6 75 15000 18000 6000	1.15
7 CTA 7 <5	-
8 CTA 8 79 16000 24000 5400	1.17

<sup>*a*</sup>[BTVS]<sub>0</sub>/[CTA]<sub>0</sub>/[AIBN]<sub>0</sub> = 200/2/1. <sup>*b*</sup>Calculated by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>*c*</sup>The theoretical molecular weight  $(M_{n,theory}) = (MW \text{ of BTVS}) \times [BTVS]_0/[CTA]_0 \times \text{conv} + (M_w \text{ of CTA}). <sup>$ *d* $</sup>Numberaverage molecular weight <math>(M_n)$  and molecular weight distribution  $(M_w/M_n)$  were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr). <sup>*e*</sup>Undetectable.

 $(M_w/M_n = 1.15 - 1.17)$  and reasonable monomer conversions (75–79%, as determined by  ${}^{1}H$  NMR spectroscopy) were obtained by the polymerization using the trithiocarbonate-type CTAs 6 and 8. RAFT polymerizations of BTVS with the dithiocarbamate-type CTA 3 also afforded a poly(BTVS) with a narrow molecular weight distribution  $(M_w/M_n = 1.18)$ . In those cases, the molecular weights of the polymer chains calculated by comparing the integrals of the peaks for the chain-end protons to those of the main-chain protons were comparable to the theoretical values, which were higher than those obtained from size exclusion chromatography (SEC) in DMF (10 mM LiBr) using polystyrene standards. Note that the thiocarbonylthio end groups (dithiocarbamate moiety for CTA 3 and dithiocarbonate moiety for CTAs 6 and 8), which correspond to the  $\omega$ -end groups derived from the Z group of CTA, were employed for the evaluation (Figures S3 and S4). Unimodal SEC peaks were detected in the SEC profiles of the poly(BTVS)s obtained with both the dithiocarbamate-type and trithiocarbonate-type mediating agents (CTAs 3, 6, and 8), as shown in Figure S8. In contrast, poly(BTVS) obtained via polymerization with the xanthate-type mediating agents (CTAs 1 and 2) had relatively broad SEC peaks  $(M_w/M_n > 1.5)$ . Using CTAs 5 and 7, extremely low monomer conversions (<5%) were obtained, and a low-molecular-weight polymer was obtained when using the dithiobenzoate-type CTA 4. RAFT polymerization of BTVS at 100 °C using V-40, 1,1'-azobis(cyclohexane-1-carbonitrile), with CTA 6 could not be controlled compared to that using AIBN at 60 °C (Table S4). Therefore, we concluded that the RAFT polymerization with CTAs 3, 6, and 8 at moderate temperature was the suitable conditions in the case of azolyl *S*-vinyl sulfide monomers.

In the next stage, the effect of the  $[CTA]_0/[AIBN]_0$  ratio on monomer conversion, molecular weights, and polydispersity of the resulting poly(BTVS)s was examined. RAFT polymerization of BTVS was conducted with CTAs 1-4, 6, and 8 at 70 °C for 24 h. The [CTA]<sub>0</sub>/[AIBN]<sub>0</sub> ratio was adjusted to be between 2 and 10, keeping the monomer/CTA molar ratio at 100/1 (Table S6). As expected, the monomer conversion decreased as the  $[CTA]_0/[AIBN]_0$  ratio increased from 2 to 10, which is consistent with the general tendency for higher CTA/ initiator ratio (lower concentration of the initiator) to lead to lower polymerization rates. In contrast, the effect of the  $[CTA]_0/[AIBN]_0$  ratio on the molecular weight distributions of the resulting poly(BTVS) was not as remarkable (Figure S9). In RAFT polymerization, the number of CTAs that have effectively fragmented and reinitiated polymerization plus the number of initiator-derived chains can contribute to the total number of polymer chains. If the initiator-derived chains are taken into account, the molecular weights of resulting polymers decrease with decreasing [CTA]<sub>0</sub>/[Initiator]<sub>0</sub> ratio when the monomer-to-CTA ratio and monomer conversion are constant. In an ideal RAFT process, however, the number of polymer chains originated from initiators should be minimal, and the number of CTA-derived chains is much larger than that of the initiator-derived chains.<sup>66,67</sup> In our system, as can be seen in Table S6, both the conversion and molecular weights decreased with increasing [CTA]<sub>0</sub>/[AIBN]<sub>0</sub> ratio, whereas the polydispersity remained narrow  $(M_w/M_n = 1.12 - 1.18$  for CTAs 6 and 8 and  $M_w/M_n = 1.18 - 1.33$  for CTA3). These results indicate that reasonable control of the polymerization of BTVS can be achieved in bulk RAFT polymerization using CTAs 3, 6, and 8 at lower CTA/initiator ratio  $([CTA]_0/[AIBN]_0 \text{ ratio} =$ 2) at 70 °C, which are optimal conditions adjusting the tradeoff between the polymerization rate and controllability of the radical polymerization.

To manipulate the molecular weights of the resulting poly(BTVS) polymers, the polymerization of BTVS was conducted at  $[M]_0/[CTA]_0$  ratios between 100 and 600, using a ratio of CTA to AIBN of 1:2 (Figure 1 and Table S7). When the polymerization of BTVS was conducted using CTA 3 in bulk at 70 °C for 24 h, a linear increase in the numberaverage molecular weights with increasing [M]<sub>0</sub>/[CTA]<sub>0</sub> ratio was observed, and the molecular weight distributions remained relatively narrow  $(M_w/M_n = 1.18 - 1.29)$  until  $[M]_0/[CTA]_0 =$ 600. A shift in the SEC trace toward higher-molecular-weight regions with a unimodal peak was seen at higher  $[M]_0/[CTA]_0$ ratios (Figure 1), demonstrating the efficient control over polymer molecular weight. A similar tendency was also observed in RAFT polymerizations of BTVS with trithiocarbonate-type mediating agents (CTAs 6 and 8). In contrast, the polymerizations with CTAs 1, 2, and 4 afforded the polymers with broad molecular weight distributions or uncontrolled molecular weights (Figure S10). Nevertheless, these results confirm the feasibility to manipulate the molecular weights of poly(BTVS)s by adjusting the monomer-to-CTA ratio in



**Figure 1.** SEC traces of poly(BTVS)s obtained by RAFT polymerization at different  $[AIBN]_0/[CTA]_0$  ratios with (a) CTA 3, (b) CTA 6, and (c) CTA 8.

RAFT polymerization with appropriate mediating agents (CTAs 3, 6, and 8) under suitable conditions.

The kinetic study of the BTVS polymerization was conducted in the presence of CTAs 3 and 6 at  $[BTVS]_0/$  $[CTA]_0/[AIBN]_0 = 200/2/1$  in bulk at 70 °C (Figure 2). On polymerization with CTA 6, a relatively high conversion (>70%) occurred after 24 h (Figure 2d). Figure 2e shows a linear increase in the number-average molecular weight, as determined by <sup>1</sup>H NMR measurements, with conversion. The theoretical molecular weight, however, was inconsistent with the experimental values determined by NMR and SEC. Nevertheless, the SEC traces of poly(BTVS) polymers obtained at different reaction times indicate a progressive increase in the molar mass with the monomer conversion and narrow unimodal SEC peaks ( $M_w/M_n = 1.12-1.15$ ). In the case of the polymerization of BTVS with CTA 3, the polymerization rate was slower than that with CTA 6 (Figure 2a). Because the polymerization was conducted in bulk, a conversion plateau was present, and this was dependent on the viscosity of the reaction mixtures and the molecular weights of the resulting polymers. Nonetheless, symmetrical unimodal SEC peaks  $(M_w/M_p =$ 1.18-1.23) without shoulders or tails were seen for the

poly(BTVS)s, as reaction proceeds up to about 60% conversion. Furthermore, the number-average molecular weight,  $M_{n\nu}$  increases in direct proportion to the conversion, as shown in Figure 2b,c. These kinetic results suggest that the polymerization of the benzothiazole-based monomer, BTVS, mediated by the CTAs 3 and 6 proceeds in a controlled manner at 70 °C under the conditions used in this study, in which unfavorable chain transfer reactions can be suppressed by the RAFT process.

RAFT Polymerization of S-Vinyl Sulfides Containing Different Azole Units. The RAFT polymerization of four Svinyl sulfide derivatives containing different azole units was also conducted at a ratio [M]<sub>0</sub>/[CTA]<sub>0</sub>/[AIBN]<sub>0</sub> of 200/2/1 at 60 °C in bulk, and the results are summarized in Table 2. Depending on the structure of the azole units, the S-vinyl sulfide derivatives showed different reactivities for RAFT polymerizations. When the polymerization of 2-TVS, which is a thiazole derivative, was carried out using with CTAs 3 and 6, poly(2-TVS)s with relatively low polydispersities  $(M_w/M_p)$  = 1.23-1.25) were obtained with reasonable conversions degree (56–68%, as determined by <sup>1</sup>H NMR spectroscopy). The same tendency was observed in RAFT polymerization of P-1,3,4-OVS, which is an oxadiazole derivative. In both cases, symmetrical unimodal SEC peaks without shoulders or tails were seen for the poly(azolyl S-vinyl sulfide) polymers obtained using CTAs 3 and 6 (Figure S11). These results agree well with those of polymerization with BTVS, in which the dithiocarbamate-type CTA 3 and the trithiocarbonate-type CTA 6 were the most efficient mediating agents to achieve controlled character of the polymerization of the azolyl S-vinyl sulfide derivatives.

In the cases of 1,3,4-TVS and M-1,3,4-TVS, which are thiadiazole derivatives, free radical polymerizations at 60 °C afforded polymers with high molecular weights and broad molecular weight distributions ( $M_n = 19\,000-43\,000, M_w/M_n =$ 1.96–2.26); however, the monomer conversions were relatively low (<35%). RAFT polymerization of 1,3,4-TVS and M-1,3,4-TVS with CTA 3 led the formation of polymers with narrow molecular weight distributions  $(M_w/M_n = 1.21-1.25)$ , while a negligible quantity of polymer was obtained when using CTA 6. In both cases, the monomer conversions in the RAFT polymerization with CTA 3 were comparable to those in free radical polymerizations, which is believed to be related to diffusion-controlled termination. Nevertheless, polymers with relatively narrow molecular weight distributions were obtained by RAFT polymerization of all azolyl S-vinyl monomers using the dithiocarbamate-type CTA 3.

The polymerization of 1,3,4-TVS was investigated kinetically with the dithiocarbamate-type CTA 3 in bulk at 60 °C and  $[M]_0/[CTA]_0/[I]_0 = 200/2/1$ . As can be seen in the time–conversion and the pseudo-first-order kinetic plots (Figure S12), only 25% conversion was reached after 24 h, the plot having a curved semilogarithmic plot; this may be due relatively high viscosity of the reaction mixture during bulk polymerization. A similar conversion "plateau" was also detected for RAFT polymerization of BTVS with CTA 3 (Figure 2a). Nevertheless, symmetrical unimodal SEC peaks ( $M_w/M_n = 1.24-1.30$ ) were detected for the poly(1,3,4-TVS)s, suggesting that the thiadiazole-based polymers with relatively low polydispersities can be obtained by RAFT polymerization of 1,3,4-TVS under suitable conditions.

Formation of Metal Complexes with Azole-Based Polymers. Synthetic polymers containing metal species are



**Figure 2.** (a, d) Time-conversion (circles) and first-order kinetic (squares) plots for polymerization of BTVS with AIBN in the presence of (a-c) CTAs 3 and (d-f) 6 ( $[BTVS]_0/[CTA]_0/[AIBN]_0 = 200/2/1$ ) in bulk at 70 °C. (b, e) Number-average molecular weights (NMR: triangles; SEC: circles) and polydispersity (squares) as a function of conversion. (c, f) SEC traces of poly(BTVS)s.

Table 2. KAFT Polymerization of 5-vinyl Sunde Derivatives Using Different CTAS in Durk at 60° C for 24	le 2. RAFT Polymerizat	on of S-Vinyl Sulfide	Derivatives Using D	Different CTAs in Bulk at (	60 °C for 24 h
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entry	monomer	CTA	$\operatorname{conv}^{b}(\%)$	$M_n^c$ (theory)	$M_n^b$ ( <sup>1</sup> H NMR)	$M_{\rm n}^{\ d}$ (SEC)	$M_{\rm w}/M_{\rm n}^{\ d}({ m SEC})$
1	2-TVS	-	73	-	_	40000	3.99
2		CTA 3	68	10000	11000	4200	1.25
3		CTA 6	56	8400	10000	3000	1.23
4	1,3,4-TVS	-	30	-	-	19000	1.96
5		CTA 3	28	3600	2800	3400	1.25
6		CTA 6	<5	-	-	-	_
7	M-1,3,4-TVS	-	34 <sup>f</sup>	-	-	43000	2.26
8		CTA 3	32 <sup>f</sup>	5300	_g	7800	1.21
9		CTA 6	0 <sup><i>f</i></sup>	-	-	-	_
10	P-1,3,4-OVS <sup>e</sup>	-	60	-	-	13000	1.53
11		CTA 3	51	11000	22000	4900	1.31
12		CTA 6	46	9700	13000	5600	1.23

 ${}^{a}$ [M]<sub>0</sub>/[CTA]<sub>0</sub>/[AIBN]<sub>0</sub> = 200/2/1.  ${}^{b}$ Calculated by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup>The theoretical molecular weight  $(M_{n,theory}) = (MW \text{ of monomer}) \times [M]_{0}/[CTA]_{0} \times (\text{conv or yield}) + (M_{w} \text{ of CTA})$ . <sup>d</sup>Number-average molecular weight  $(M_{n})$  and molecular weight distribution  $(M_{w}/M_{n})$  were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr). <sup>e</sup>Polymerization in DMF (10 mmol/mL). <sup>f</sup>Yield: methanol-insoluble part. <sup>g</sup>Undetectable.

functional materials with a wide range of applications.<sup>68-70</sup> In this study, the preparation of metal complexes was carried out between the resulting azole-based polymers and MCl<sub>2</sub> (M = Cu, Ni, and Zn) in DMF at 80 °C for 24 h (Scheme 2) according to the previous literature.<sup>26</sup> The results are summarized in Table 3. When complex formation was carried

out at a 1:1 molar ratio of the BTVS unit and metal species  $(MCl_2)$ , the poly(BTVS)-metal complexes were obtained with reasonable yields (43–57%), and they showed various colors, depending on the nature of the metal (Figure S13). The metal contents were estimated to be 11, 0.16, and 0.50 wt % in poly(BTVS)-Cu, poly(BTVS)-Ni, and poly(BTVS)-Zn, respec-

Table 3. Formation of Poly(BTVS)-Metal Complexes at 80 °C for 24  $h^a$ 

entry	metal <sup>a</sup>	thiazole unit:M	yield <sup>b</sup> (%)	$\begin{array}{c} M \ cont^{c} \\ (wt \ \%) \end{array}$	M cont (mol %)	appearance
1	Zn	1:1	51	0.50	1.5	light yellow
2	Ni		57	0.16	0.54	brown
3	Cu		43	11	28	dark brown
4	Zn	1:5	22	1.8	5.2	yellow
5	Ni		22	0.90	2.9	dark brown
6	Cu		16	2.3	6.5	dark brown

<sup>a</sup>Zn:ZnCl<sub>2</sub>, Ni:NiCl<sub>2</sub>, Cu:CuCl<sub>2</sub>. <sup>b</sup>Methanol-insoluble part. <sup>c</sup>Determined by ICP.

tively, determined by inductive-coupled plasma mass (ICP-MS) measurements. The obtained ICP analysis indicated that the benzothiazole rings were coordinated more strongly to copper ions than to either nickel or zinc species.

Figure 3 shows FT-IR spectra of the pristine poly(BTVS), poly(BTVS)-Cu, poly(BTVS)-Ni, and poly(BTVS)-Zn com-



**Figure 3.** FT-IR spectra of poly(BTVS) and metal complexes. Lower figure: magnification in the range of 1800-500 cm<sup>-1</sup>.

plexes. Characteristic peaks between 725 and 755 and 1502 cm<sup>-1</sup> are seen for poly(BTVS), which may be attributed to the thioether C–S bond and the thiazole ring, respectively. Characteristic vibrations have been reported previously; for example, the C–S bond<sup>71</sup> and thiazole ring<sup>26</sup> are indicated by peaks at 750 and 1535 cm<sup>-1</sup>. In the spectrum of poly(BTVS) obtained after Cu complexation, the peak attributed to the thiazole ring at 1502 cm<sup>-1</sup> almost disappeared, suggesting that the thiazole ring contributes to the complexation with copper species. In addition, a new peak at around 1670 cm<sup>-1</sup> is also detected in the poly(BTVS)–Cu complex, which may correspond to the C=N stretch in the benzothiazole unit shifting after complexation with the metal atom. In contrast, both poly(BTVS)–Ni and poly(BTVS)–Zn showed no significant changes in their FT-IR spectra, suggesting that the

nature of the metal species significantly affects the progress of the coordination reactions. Furthermore, the solubility of the obtained complexes changed compared to pristine poly(BTVS) (Table S8), which should result from the formation of the complexes (poly(BTVS)–Cu, poly(BTVS)–Ni, and poly-(BTVS)–Zn, respectively).

From dynamic light scattering (DLS) analysis, the hydrodynamic diameter distribution  $(D_{\rm h})$  of the pristine poly-(BTVS), poly(BTVS)-Cu, poly(BTVS)-Ni, and poly-(BTVS)-Zn complexes prepared at BTVS unit/MCl<sub>2</sub> = 1/1 molar ratio were estimated to be 9.7, 730, 8.0, and 4.5 nm in DMF, respectively (Figure S14a). The much larger  $D_{\rm b}$  value of poly(BTVS)-Cu should result from aggregation due to the stronger coordination, consistent with the ICP analysis. In the poly(BTVS)-Cu system, many kind of complexes may exist because of a variety of coordination (i.e., inter- and intrachain coordination). Even though DLS has the single peak, the peak has dispersibility; in that regard, the aggregate is a mixture of several regimes with ca. 200-1100 nm. When complex formation was conducted at higher metal content (BTVS unit/MCl<sub>2</sub> = 1/5 molar ratio), the yields of the products were relatively low (yield <25%), and the metal content increased slightly for the complexes of poly(BTVS)-Ni and poly-(BTVS)-Zn and decreased for the poly(BTVS)-Cu. The DLS result of the complex prepared at BTVS unit/CuCl<sub>2</sub> = 1/5exhibited bimodal distributions (Figure S14b), suggesting that the composition in the feed affects size and size distributions of the polymer-Cu complexes. As can be seen in Table 4, the

Table 4. Formation of Poly(S-vinyl sulfide)–Cu Complexes at 80 °C for 24  $h^{a}$ 

entry	polymer	yield <sup>b</sup> (%)	$\begin{array}{c} M \ cont^c \\ (wt \ \%) \end{array}$	M cont (mol %)
1	poly(BTVS)	43	11	28
2	poly(2-TVS)	23	11	22
3	poly(1,3,4-TVS)	58	8.4	17
4	poly(M-1,3,4-TVS)	62	19	38
5	poly(P-1,3,4-OVS)	46	8.6	23
a 1 1 -	·····: M 11 M C···Cl	bx	<b>1</b> : <b>1 1</b>	Dul human

"Azole unit:M = 1:1, M:CuCl<sub>2</sub>. "Methanol-insoluble part. Dark brown product was obtained in all cases. "Determined by ICP.

metal contents of poly(2-TVS)–Cu, poly(1,3,4-TVS)–Cu, poly(M-1,3,4-TVS)–Cu, and poly(P-1,3,4-OVS)–Cu (8.4–19 wt %) prepared at the monomer unit/CuCl<sub>2</sub> = 1/1 molar ratio were comparable to that of poly(BTVS)–Cu (11 wt %), suggesting that these azole units have ability to coordinate to copper species.

Optical and electrochemical behaviors of the metal complexes were investigated by UV–vis absorption, fluorescence, and cyclic voltammetry (CV) measurements. The UV– vis absorption and fluorescence measurements were carried out in DMF, and we confirmed, visually, that all the complexes were soluble, forming homogeneous solutions. In UV–vis spectra of poly(BTVS) and the metal complexes (Figure 4a), poly(BTVS) had an absorption band due to the benzothiazole units below 300 nm; in contrast, the absorption peaks of poly(BTVS)–Cu, poly(BTVS)–Ni, and poly(BTVS)–Zn complexes were red-shifted compared to that of poly(BTVS). This changes in the UV–vis spectra resulted from the elongation of the conjugated structure due to the coordination between benzothiazole rings and metal species (N···M<sup>2+</sup>···S). In



Figure 4. (a, c) Absorption and (b, d) fluorescence spectra of (a, b) poly(BTVS), poly(BTVS)–Cu, poly(BTVS)–Ni, and poly(BTVS)–Zn complexes (the excitation wavelengths were 302, 340, 365, and 365 nm, respectively) and (c, d) poly(BTVS)–Cu (Cu content = 11 and 2.9 wt % for blue and red lines, respectively; excitation wavelength was 340 nm) in DMF solutions (concentration = 0.1 mg/mL).

the fluorescence spectra, the metal complexes exhibited fluorescence due to the elongation of the conjugated structure; in particular, strong fluorescence was observed in poly-(BTVS)–Cu (Figure 4b). Interestingly, the fluorescence spectra of poly(BTVS)-Ni and poly(BTVS)-Zn changed after 24 h, whereas no significant change was observed in the fluorescence spectrum of poly(BTVS)-Cu (Figure S15). This result suggests that complexes formed on coordination to copper species are more stable than those formed on coordination to zinc and nickel species in poly(BTVS). For poly(BTVS)-Cu, the relationship between fluorescence behavior and metal content in the complex was investigated in detail. In the fluorescence spectra of two poly(BTVS)-Cu (Cu content = 2.9 and 11 wt %), maximum emissions were observed at 421 and 491 nm in poly(BTVS)-Cu (Cu content = 2.9 wt %) and poly(BTVS)-Cu (Cu content = 11 wt %), respectively (Figure 4d). The higher metal content led to peaks being more red-shifted in the UV-vis spectra (Figure 4c). This shift suggests that the metal content is the dominant driving force that leads to a longer conjugated structure, resulting in differences in the fluorescence behaviors of the complexes. Therefore, the stability of the fluorescence signals, which occur on complexation of poly(BTVS) with metal species, can be controlled by selecting the correct metal species and the metal content.

We also investigated the UV–vis absorption and fluorescence behaviors of metal complexes using poly(2-TVS), poly(1,3,4-TVS), poly(M-1,3,4-TVS), and poly(P-1,3,4-OVS) with copper species in DMF. As well as the metal complexes with poly(BTVS), four metal complexes with copper species had different spectra compared to the pristine polymers (Figure 5); this may be due to the coordination of polymer to copper species. Unfortunately, the complexes did not exhibit the same strong fluorescence as poly(BTVS)–Cu.



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Figure 5. (a) Absorption and (b) fluorescence (excitation wavelength: 340 nm) spectra of complexes of the azole-based polymers with copper in DMF (concentration = 0.1 mg/mL).

The electrochemical properties of the metal complexes with copper species were investigated by the CV measurements (Figure 6). Each experiment was carried out in the degassed DMSO (or DMF) solutions with 0.1 M tetrabutylammonium hexafluorophosphate under the nitrogen atomosphere. The pristine polymers, poly(BTVS), poly(2-TVS), poly(1,3,4-TVS), poly(M-1,3,4-TVS), and poly(P-1,3,4-OVS), showed clear reduction waves due to the electron-deficient azole units. In the previous work by Beloglazkina and co-workers, copper complex with the benzothiazole-based molecule exhibited the higher reduction potential in comparison to the pristine benzothiazole-based molecule.<sup>72</sup> As can be seen in Figure 6a, the reduction potential of poly(BTVS)-Cu was observed at 0.04 V whereas the pristine poly(BTVS) showed the reduction potential of -0.08 V. The reduction potential of poly(2-TVS) was also shifted from -0.01 to 0.03 V after the coordination with copper species (Figure 6b). The change of CV behaviors was detected in poly(1,3,4-TVS), poly(M-1,3,4-TVS), and poly(P-1,3,4-OVS). Their CV behaviors were different from those of poly(BTVS) and poly(2-TVS), which should result from the structural factor of the azole units. Consequently, the obtained electrochemical results supported the formation of the metal complexes with copper species. In these systems, each redox event is attributed to a mixture of several complexes formed through coordination between inter- and intrachains.

Then, DLS analysis was used to investigate the metal complexes formed with copper species. As can be seen in Figure 7a, the  $D_h$  value of poly(BTVS) shifted to the larger values after complexation with copper species, which could be due to aggregation caused by the strong coordination between poly(BTVS) and copper species. Poly(2-TVS)–Cu and poly(P-1,3,4-OVS)–Cu showed similar DLS behavior to that of poly(BTVS) (Figure 7b,e), whereas poly(1,3,4-TVS)–Cu and poly(M-1,3,4-TVS)–Cu had bimodal DLS profiles, indicating

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Figure 6. CV profiles of pristine polymers (blue line) and complexes with copper (red line) of (a) poly(BTVS), (b) poly(2-TVS), (d) poly(M-1,3,4-TVS), and (e) poly(P-1,3,4-OVS) in DMF and (c) poly(1,3,4-TVS) in DMSO at 25 °C (concentration = 2.0 mg/mL).

that the  $D_h$  values correspond to pristine polymers and aggregates (Figure 7c,d). These results demonstrate that the structure of azole units in polymers was the most important factor controlling the coordination ability to the metal species. In the thermogravimetric analysis (Figure S16), decomposition began at around from 240 °C in poly(BTVS). On the other hand, the metal complexes poly(BTVS)–Cu, poly(BTVS)–Ni, and poly(BTVS)–Zn exhibited high thermal stability, as did the pristine polymer.

After the discovery of the relevance of Cu-thioether bonds in blue copper proteins, a large number of compounds containing thioether groups have been developed to investigate complexation with Cu species.45-48 For example, various imidazole compounds containing the thioether group were investigated, in which both the imidazole nitrogen atom and the thioether sulfur atom act as donor components to afford copper complexes.<sup>45,48</sup> In mainly blue copper proteins, the orbital containing an unpaired electron of Cu(II) overlaps with histidine and cysteine moieties.<sup>45,46</sup> Concerning color, the deep blue color is reported to be caused by charge transfer in the Cu-thiolate bond in the blue copper proteins.<sup>46</sup> In our system, both nitrogen atoms of the benzothiazole ring and sulfur atom of the thioether moiety in the monomer unit (BTVS) may chelate with Cu species via intramolecular and intermolecular complexation. To understand the complex formation between poly(BTVS) and Cu species, the behavior of complex formation between BTVS monomer and CuCl<sub>2</sub> with the several different [BTVS]/[CuCl<sub>2</sub>] ratios was



Figure 7. DLS traces of pristine polymers (blue line) and complexes with copper (red line) of (a) poly(BTVS), (b) poly(2-TVS), (d) poly(M-1,3,4-TVS), and (e) poly(P-1,3,4-OVS) in DMF and (c) poly(1,3,4-TVS) in DMSO at 25  $^{\circ}$ C (concentration = 2.0 mg/mL).

investigated under the same procedure as that between poly(BTVS) and  $CuCl_2$ . According to the job plot from the experiments (Figures S17and S18), the formation of 1:1 complex was plausible. Furthermore, the intermolecular complexation may contribute to the formation of aggregated, network structures (Figure 8a); in contrast, intramolecular complexation may lead to the production of metallopolymers without significant changes in the morphology and assembled structures.

Synthesis of Block Copolymers and Metal Complexation. Block copolymers containing metal centers, so-called metalloblock copolymers, have attracted much interest as new functional materials with characteristic assembled architectures.<sup>69,73</sup> Here, we developed novel metalloblock copolymers by complexing metal species with azole-based block copolymers. For the purpose, we synthesized block copolymers by RAFT polymerization of styrene (St) using poly(BTVS) as a macro-CTA (Scheme 3a). As mentioned in a previous section, the controlled radical polymerization of BTVS could be achieved using the trithiocarbonate-type CTA 6, which is an effective CTA with high chain transfer constant, in controlled radical polymerization of conjugated monomers, such as St. Therefore, trithiocarbonate-terminated poly(BTVS)s with low molecular weights were initially prepared by RAFT polymerization of BTVS with CTA 6. Then, the resulting macro-CTAs were employed for block copolymer synthesis. As shown in Table 5, the CTA-to-initiator ratio  $([macro-CTA]_0/[AIBN]_0)$ was held constant at 2, while the monomer-to-CTA ratio  $([St]_0/[poly(BTVS) macro-CTA]_0)$  was varied from 50 to 400

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Figure 8. Postulated structures of (a) poly(BTVS)-Cu complexes and (b) assembled structures of the benzothiazole-based block copolymer and metalloblock copolymer in ethyl acetate (EtOAc) and THF.

Scheme 3. Synthesis of Block Copolymers by RAFT Polymerization of Styrene Using Poly(azoyl S-vinyl sulfide) Macro-CTAs



to control the comonomer content and molecular weight. Under these conditions, the targeted block copolymers were obtained in high yields (yield >85%) with relatively narrow molecular weight distributions ( $M_w/M_n = 1.26-1.44$ ). The molecular weights of the benzothiazole-based block copolymers evaluated from the compositions determined by elemental analysis and the molecular weights of the poly(BTVS) macro-CTAs were comparable to the theoretical values. The SEC chromatograms of the starting macro-CTA and growth polymers showed that the molecular weight clearly shifted to higher molecular weights at higher [St]<sub>0</sub>/[macro-CTA]<sub>0</sub> ratios (Figure 9a). These results clearly demonstrate the successful synthesis of poly(BTVS)-*b*-poly(St) block polymers, in which

one segment has the ability to coordinate to various metal species.

The same synthetic strategy was used for the synthesis of block copolymers composed of 2-TVS and St, in which RAFT polymerization of St was conducted using poly(2-TVS) as a macro-CTA, as shown in Scheme 3b. The thiazole-based block copolymers, poly(2-TVS)-*b*-poly(St)s, with predetermined molecular weights and relatively low polydispersities ( $M_{n,SEC}$  = 8400–35 000,  $M_w/M_n$  = 1.16–1.30) were obtained with reasonable yields (60–82%, Table 5). Increasing the monomer-to-macro-CTA ratio leads to a shift in the SEC trace toward higher molecular weights with no significant homopolymer impurity (Figure 9b), clearly demonstrating efficient block formation. Thus, chain extension from the trithiocarbonate-

Table 5. Synthesis of Block Copolymers by RAFT Polymerization of Styrene Using Poly(azoyl S-vinyl sulfide) Macro-CTAs for 24 h in  $Bulk^a$ 

entry	macro-CTA	$[M]_0/[Macro-CTA]_0$	yield <sup>b</sup> (%)	$M_n^c$ (theory)	$M_n^d$ (EA)	$M_n^{e}$ (SEC)	$M_{\rm w}/M_{\rm n}^{\ e}~({ m SEC})$	composition <sup>d</sup> BTVS:St
1 <sup>f</sup>	poly(BTVS) <sup>h</sup>	50	87	8000	5800	9000	1.36	45:55
2 <sup>f</sup>		100	96	13000	9100	16000	1.30	25:75
3 <sup>f</sup>		200	94	23000	15000	28000	1.29	14:86
4 <sup>f</sup>		400	92	42000	22000	52000	1.26	9:91
5 <sup>f</sup>	poly(BTVS) <sup><i>i</i></sup>	100	91	16000	12000	17000	1.39	42:58
6 <sup>f</sup>		200	95	26000	17000	28000	1.44	26:74
7 <sup>g</sup>	poly(2-TVS) <sup>j</sup>	50	70	7100	4000	8400	1.30	77:23
8 <sup>g</sup>		100	81	12000	5300	14000	1.21	49:51
9 <sup>g</sup>		200	82	20000	7700	27000	1.16	30:70
$10^g$		400	60	28000	11000	35000	1.22	19:81

<sup>*a*</sup>[Macro-CTA]<sub>0</sub>/[AIBN]<sub>0</sub> = 2. <sup>*b*</sup>Hexane-insoluble part. <sup>*c*</sup>The theoretical molecular weight  $(M_{n,theory}) = (MW \text{ of } St) \times [St]_0/[Macro-CTA]_0 \times yield + (MW \text{ of } Macro-CTA).$  <sup>*d*</sup>Calculated by elemental analysis (EA). <sup>*c*</sup>Measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr). <sup>*f*</sup>Polymerization at 70 °C. <sup>*g*</sup>Polymerization at 60 °C. Poly(BTVS) macro-CTA. <sup>*h*</sup> $M_{n/SEC} = 3500$ ,  $M_w/M_n = 1.21$ . <sup>*i*</sup> $M_{n/SEC} = 6800$ ,  $M_w/M_n = 1.13$ . <sup>*j*</sup>Poly(2-TVS) macro-CTA:  $M_{n,SEC} = 3400$ ,  $M_w/M_n = 1.20$ .



**Figure 9.** SEC traces (DMF + 10 mM LiBr) of (a) poly(BTVS)-*b*-poly(St)s and poly(BTVS) macro-CTA ( $M_{n,SEC}$  = 3500,  $M_w/M_n$  = 1.21) and (b) poly(2-TVS)-*b*-poly(St)s and poly(2-TVS) macro-CTA ( $M_{n,SEC}$  = 3400,  $M_w/M_n$  = 1.20). See Table 5 for detailed polymerization conditions.

terminated poly(azolyl S-vinyl sulfide) macro-CTAs to St can be successfully achieved under the conditions, providing azolebased block copolymers with an as-designed chain structure and narrow molecular weight distributions.

The selective complexation of metal species  $(CuCl_2)$  with the benzothiazole-based block copolymer (BTVS:St = 42:58) was carried out at a molar ratio of BTVS unit/CuCl<sub>2</sub> = 1:1 in DMF at 80 °C for 24 h. In this study, we focused on how selective complexation of the metal species with the poly(BTVS) segments in the block copolymers lead to changes in selfassembled structures and characteristic fluorescent properties. Complexation-responsive assembled structures of the block copolymers were characterized using DLS in ethyl acetate and THF. Note that poly(BTVS) was soluble in THF and insoluble in ethyl acetate. Poly(St) was soluble in both solvents. In contrast, the poly(BTVS)/Cu complex did not dissolve well in either solvent. As can be seen in Figure 10a, a relatively narrow



Figure 10. (a, b) DLS traces and (c, d) fluorescence (excitation wavelength: 340 nm) spectra of poly(BTVS)-*b*-poly(St) and poly(BTVS)/Cu-*b*-poly(St) (BTVS: St = 42:58) in (a, c) ethyl acetate and (b, d) THF at 25  $^{\circ}$ C (concentration = 2.0 mg/mL).

hydrodynamic diameter distribution ( $D_{\rm h}$  = 177 nm) of the benzothiazole-based block copolymer was observed in ethyl acetate, indicating the formation of micelles consisting of an insoluble poly(BTVS) core and soluble poly(St) shell. After complexation with Cu species, the metalloblock copolymer, poly(BTVS)/Cu-b-poly(St), showed a remarkable decrease in the hydrodynamic diameter ( $D_{\rm h}$  = 109 nm), which may be due to core shrinkage that occurs on complexation. Figure 10c shows the fluorescence spectra of the block copolymer before and after complexation in ethyl acetate. In the case of poly(BTVS)/Cu-b-poly(St), the maximum emission occurs at 421 nm, suggesting that the elongation of the conjugated structure by the complexation with Cu species occurs even in the core part of the self-assembled structures. In the DLS spectrum of poly(BTVS)-b-poly(St) in THF, as expected, smaller species  $(D_h < 10 \text{ nm})$  were detected (Figure 10b),

indicating that pristine block copolymer exists in the unimolecularly dissolved state, whereas the poly(BTVS)/Cub-poly(St) shows bimodal DLS peaks, corresponding to the presence of unimers and larger aggregates. In the fluorescence spectra, there was no significant effect of the solvent on the peak intensity and position (Figure 10d). A similar tendency was observed in the metalloblock copolymer prepared from the benzothiazole-based block copolymer with different comonomer compositions (BTVS:St = 26:74) (Figure S19). These results suggest that the poly(BTVS)/Cu-b-poly(St) are composed of two components (Figure 8b); the small species observed by DLS in THF is interpreted as a loose poly(BTVS)/Cu complex, in which the complexation between the Cu and poly(BTVS) segment takes place around single poly(BTVS) chain to afford an intramolecular complex. The larger species may correspond to a tight poly(BTVS)/Cu complex, in which Cu species interacts tightly with the poly(BTVS) segment via intermolecular complexation.

# CONCLUSION

In summary, this work presents a straightforward synthetic approach to prepare heterocyclic S-vinyl monomers with diverse azole structures. These can undergo controlled radical polymerization via RAFT process. Both the dithiocarbamatetype CTA 3 and trithiocarbonate-type CTA 6 were efficient in achieving controlled polymerization of the thiazole-based monomers (BTVS and 2-TVS) and oxadiazole-based monomer (P-1,3,4-OVS), whereas only the dithiocarbamate-type CTA 3 was effective for the thiadiazole-based monomers (1,3,4-TVS and M-1,3,4-TVS) to afford azole-based polymers with relatively narrow molecular weight distributions and predetermined molecular weights. The resulting poly(S-vinyl sulfide) polymers containing azole units in the side chain acted as novel polymeric ligands for metal complex formation. The formation of complexes between the thiazole-containing polymers with various metal species (ZnCl<sub>2</sub>, NiCl<sub>2</sub>, and CuCl<sub>2</sub>) led to the characteristic optical properties, which were evaluated by absorption and fluorescence in organic solvents. The polymer-metal complexes exhibited red-shifted absorption peaks, which may be due to the expansion of the  $\pi$ -conjugated system. In particular, the poly(BTVS)-Cu complex exhibited the fluorescence in the range of ca. 350-600 nm, whereas the poly(BTVS) showed no fluorescence. We also developed novel metalloblock copolymers by complexation of metal species with azole-based block copolymers, affecting the self-assembled structures and characteristic fluorescent properties. This work opens new avenues to extend the range of azole-based polymers and their metal complexes with various functions and properties, in which the chemical structures, topologies, and assembled structures can be manipulated by controlled radical polymerization of a new family of S-vinyl monomers, azolyl Svinyl sulfides.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b02573.

Figures showing <sup>1</sup>H and <sup>13</sup>C NMR spectra of the monomers and polymers, GPC traces of the resulting polymers, kinetic results of the polymerization of 1,3,4-TVS, thermogravimetric analysis of the products, photo-

graphs, DLS traces, and fluorescence spectra of complexes, and tables summarizing the solubility of the products, polymerization results under various conditions, metal contents and solubility of the complexes (PDF)

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#### Notes

The authors declare no competing financial interest.

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