Macromolecules

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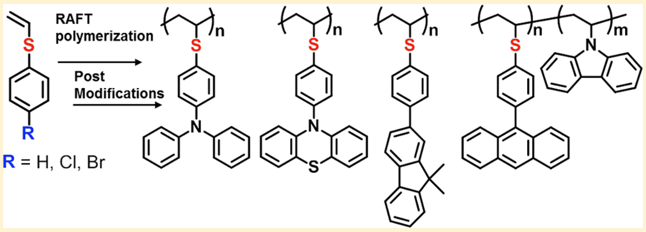
RAFT Polymerization of *S*-Vinyl Sulfide Derivatives and Synthesis of Block Copolymers Having Two Distinct Optoelectronic Functionalities

Kazuhiro Nakabayashi,[†] Yohei Abiko,[‡] and Hideharu Mori*,[†,‡]

[†]Department of Polymer Science and Engineering and [‡]Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan

Supporting Information

ABSTRACT: Well-defined sulfur-containing polymers and block copolymers were synthesized by reversible addition−fragmentation chain transfer (RAFT) polymerization of *S*-vinyl sulfide derivatives, in which the thioether moiety is directly connected to the vinyl group. We initially investigated RAFT polymerization of four different *S*-vinyl sulfide derivatives, phenyl vinyl sulfide (PVS), 4-chlorophenyl vinyl sulfide (CPVS), 2,4-dichlorophenyl vinyl sulfide (DCPVS), and 4-bromophenyl vinyl sulfide (BPVS). Three xanthate-type chain transfer agents (CTAs), a dithiocarbamate-type CTA, and a dithioester-type CTA were compared for these RAFT polymerizations. Reasonable control of the polymerization of PVS was confirmed by an observed linear increase in the molecular weight with the conversion, feasibility to control molecular weight based on the ratio of monomer consumed to the amount of CTA used, chain end structure determined by ^{1}H NMR, and chain extension experiment. The RAFT polymerization of the bromo-substituted monomer (BPVS) also proceeded in the controlled fashion under the same conditions. Incorporation of optoelectronic groups, including anthracene, fluorene, diphenylamine, and phenothiazine on the bromophenyl pendant group of poly(BPVS) were accomplished by palladium-catalyzed postmodifications. We also investigated characteristic optoelectronic properties of modified polymers and block copolymers with two distinct electronic functionalities.



INTRODUCTION

Sulfur-containing polymers derived from vinyl monomers have attracted a great deal of attention, due to their potential applications in numerous areas in polymer resseach. For example, sulfur-containing substituents, including linear thioether and cyclic thiophene, are the most commonly used groups for increasing a materials refractive index. Sulfur-containing (meth)acrylates, a prevalent material for this purpose, have a wide variety of applications in plastic lenses, optical disc substrates, optical adhesives or encapsulants, antireflective coatings, and photoresists.[1] Thioether-containing styrene derivatives have been previously prepared for surface-enhanced Raman scattering-encoded polymers for combinatorial screening and biomedical diagnostics.[2] Thioether-containing styrene has also been employed for the synthesis of gold nanocomposites via chemisorption of gold nanoparticles onto the thioether groups on the polymer side chains.[3] So far, a variety of polystyrene and poly(meth)acrylate derivatives with sulfur-containing side chains have been reported, and most of these sulfur-containing polymers were traditionally prepared by conventional radical polymerizations.

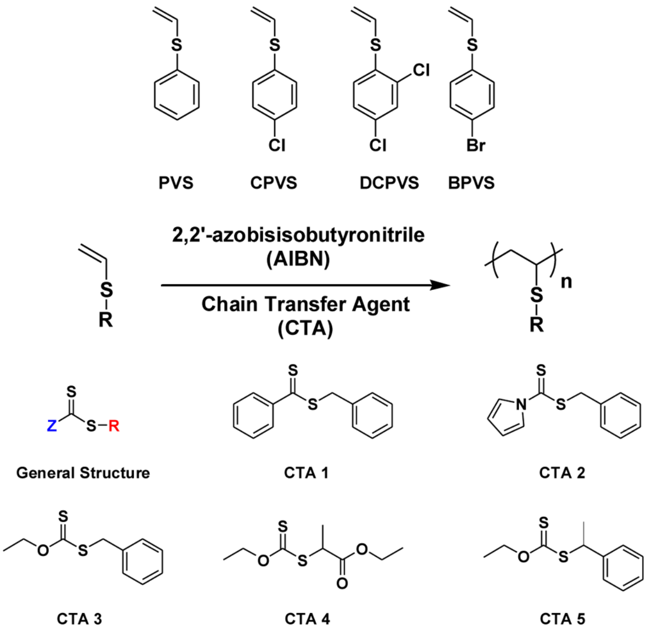
Recently, the controlled radical polymerization (also known as controlled/“living” radical polymerization or reversible deactivation radical polymerization) of sulfur-containing vinyl monomers has gained considerable interest, driven by the remarkable development of thiol−disulfide chemistry. Traditionally, so-called iniferter system using styrene derivatives with a dithiocarbamate moiety, which can also act as a photoiniferter (photoinitiator−transfer agent−terminator),[4] have been employed for the synthesis of graft copolymers[5] and hyperbranched polymers.[6] A sulfur−sulfur cross-linked polymer was previously synthesized from a similar styrene derivative with a dithiocarbamate as a source of dormant radicals, in which the dithiocarbamyl residue is the polymerizable part of the molecule.[7] Similar methacrylate-type monomers bearing the dithiocarbamate photoiniferter moiety have been also reported.[8,9] Reversible addition−fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP) of pyridyl disulfide ethyl methacrylate afforded functional polymers having pendant pyridyl disulfide reactive groups, which were employed as simultaneous and reversible functionalization[10] to generate functional nano-objects, such as reversibly cross-linked micelles,[11] protein−polymer particles,[12] and nanoparticles with biocompatible shells.[13] ATRP and RAFT polymerization of disulfide−based di(meth)acrylates, which can be regarded as cross-linking agents, have been employed for the synthesis of branched acrylic copolymers,[14] cross-linked (bio)degradable nanogels,[15] thiol-functionalized

Received: April 20, 2013
Revised: July 3, 2013

block copolymer vesicles,[16] and thiol/disulfide-functionalized star polymers.[17] A variety of block copolymers having a polythiol segment were synthesized by RAFT polymerization of vinyl monomers with protected thiol groups, involving a methacrylate carrying a xanthate moiety,[18] (meth)acrylamides and (meth)acrylates with a 2-nitrobenzylthioether moiety,[19,20] and (meth)acrylates with an acetyl thioalkyl group.[21] Other interesting systems involve the radical ring-opening polymerization of sulfur-containing cyclic vinyl monomers, such as cyclic allyl sulfide derivatives,[22,23] which can afford functional polymers with sulfur atom in the polymer backbones.

Here, we present the first example of controlled synthesis of sulfur-containing polymers by RAFT polymerization of *S*-vinyl monomers, phenyl vinyl sulfide (PVS) derivatives (Scheme 1) that have thermal and chemical stability as well as the structural versatility. Differing from styrene, (meth)acrylate, and (meth)-acrylamide-type monomers, the direct linkage of the sulfur atom to the vinyl group is an important feature of these monomers, because it may affect not only the polymerization behavior but also various properties of the resulting polymers. The development of a new *S*-vinyl monomer family, which is applicable for controlled radical polymerization and can be regarded as an analogous of vinyl ether, would represent a significant advance in the field of functional polymeric materials. An attractive feature of PVS derivatives is the structural diversity through the reaction of 1,2-dibromoethane with thiol compounds having various substituted groups, and the feasibility to act as building blocks and functional units for the construction of new macromolecules.

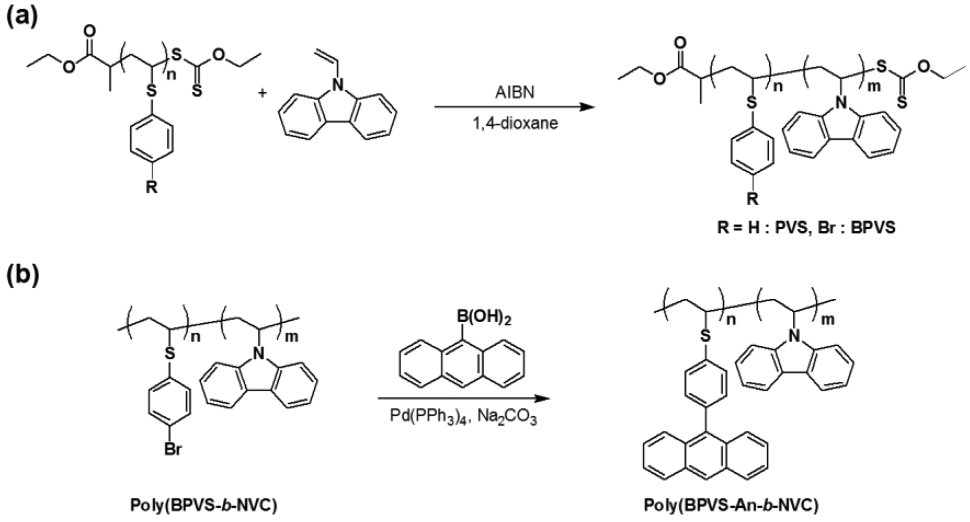
Scheme 1. Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization of *S*-Vinyl Sulfide Derivatives Using Different Chain Transfer Agents (CTAs)



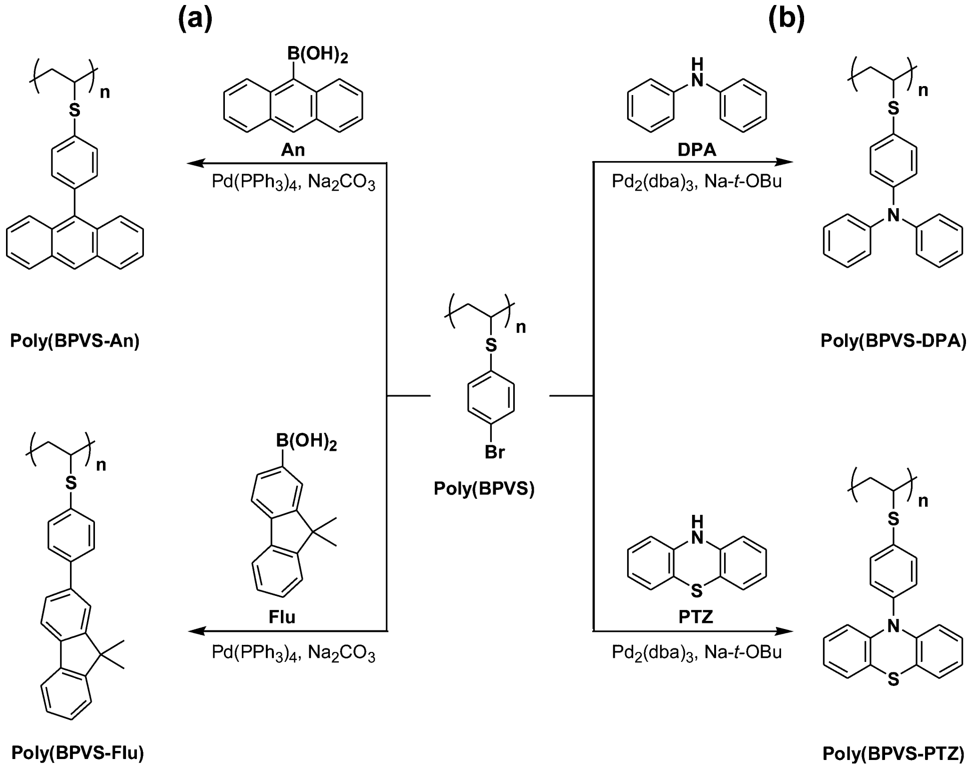
Several reports have been published on conventional radical polymerization of *S*-vinyl sulfides.[24−28] Price and Morita reported radical copolymerization of PVS with various comonomers including styrene and methyl acrylate, and indicated the importance of the 3d orbital resonance between the sulfur atom and the adjacent carbon atom in the transition state of copolymerization reactions.[24] They demonstrated that PVS was comparable in reactivity to methyl vinyl sulfide, with Q and e values of PVS measured as $Q = 0.32$, $e = -1.4$. Otsu et al. reported radical polymerization of *p*-substituted PVS derivatives to clarify the effect of the sulfur atom and substituent group.[25] They indicated that the higher reactivity of vinyl sulfide relative to vinyl ether might be explained by the 3d orbital resonance between the propagating radical and the adjacent sulfur atom in vinyl sulfide.[29] Since vinyl sulfides are typical electron donating monomers, alternating copolymerizations with electron accepting monomers, such as maleic anhydride,[30,31] acrylonitrile,[32] and maleimide,[33] have been reported as taking place on the basis of donor−acceptor interactions. Poly(PVS) was also employed as a precursor for the synthesis of poly(vinylsulfonium salts).[34]

In this study, RAFT polymerization of *S*-vinyl sulfide derivatives, regarded as an important class of *S*-vinyl monomers, were employed for the synthesis of sulfur-containing polymers and block copolymers with an as-designed chain structure and narrow molecular weight distribution. In the first part, we

Scheme 2. (a) Synthesis of Block Copolymers by RAFT Polymerization of NVC Using Poly(*S*-vinyl sulfide) Macro-CTAs and (b) Postmodification of Poly(BPVS-*b*-NVC)



Scheme 3. Postmodifications of Poly(BPVS) by (a) Suzuki Coupling Reaction and (b) Buchwald−Hartwig Coupling Reaction



briefly compared RAFT polymerization behavior of four *S*-vinyl sulfide derivatives: phenyl vinyl sulfide (PVS), 4-chlorophenyl vinyl sulfide (CPVS), 2,4-dichlorophenyl vinyl sulfide (DCPVS), and 4-bromophenyl vinyl sulfide (BPVS), as shown in Scheme 1. Recent progress in RAFT polymerization processes has allowed for the synthesis of well-defined polymers by radical polymerization of nonconjugated monomers. In particular, dithiocarbonates (xanthates) are known to be useful for controlling the radical polymerization of nonconjugated *O*-vinyl and *N*-vinyl monomers. On the basis of the Q and e values of PVS ($Q = 0.32$, $e = -1.4$), the reactivities of *S*-vinyl sulfide derivatives are considered to be comparable to that of *N*-vinylcarbazole (NVC, $Q = 0.26$, $e = -1.29$), which is a representative nonconjugated *N*-vinyl monomer having a pendant electron-donating carbazolyl moiety. With this in mind, we attempted to find a suitable CTA and conditions to provide the controlled radical polymerization of *S*-vinyl sulfide derivatives. The controlled character of RAFT polymerization of the selected monomers, PVS and BPVS, was investigated using the optimized conditions. Then, we conducted the synthesis of block copolymers by RAFT polymerization of NVC using poly(PVS) as a macro-CTA (Scheme 2). Regardless of the potentially interesting properties of the resulting products, the synthesis of a well-defined block copolymer composed of poly(PVS) and poly(NVC) is challenging, owing to the low reactivity of both nonconjugated monomers and the low stability of the propagating radicals. The effects of the order of block construction and composition of the second monomer to the macro-CTA were studied in detail, in terms of the controlled character of the polymerization and feasibility to manipulate the structures of the resulting block copolymers. Next, the synthesis of well-defined block copolymers was conducted by RAFT polymerization of BPVS using macro-CTA. The incorporation of optoelectronic groups on the bromophenyl unit were conducted by palladium-catalyzed postmodifications to afford functional polymers with additional optoelectronic moieties, such as anthracene (An), fluorene (Flu), diphenylamine (DPA), and phenothiazine (PTZ), in the side chain (Scheme 3). The postmodification of poly(NVC)-*b*-poly(BPVS) also afforded a block copolymer incorporating two distinct electronic functionalities (Scheme 2b). We believe that this synthetic approach and resulting polymers represent a new paradigm, which will significantly extend to range of functional materials composed of nonconjugated *S*-vinyl and *N*-vinyl monomers with characteristic optoelectronic properties.

■ EXPERIMENTAL SECTION

Materials. 2,2-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. 4-Chlorobenzenethiol (TCI, >98%), 2,4-dichlorobenzenethiol (TCI, >97%), 4-bromobenzenethiol (TCI, >97%), sodium ethoxide (ca. 20% in ethanol, TCI), 1,2-dibromoethane (TCI, >99%), 9-anthraceneboronic acid (TCI), 9,9-dimethylfluoren-2-boronic acid (TCI) diphenylamine (TCI, >99%), phenothiazine (TCI, >98%), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$, TCI, >97%), tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$, TCI, >75%), and sodium carbonate (Wako, >99%), were used as received. Phenyl vinyl sulfide (PVS, TCI, >98%) used as a monomer was purified by distillation under reduced pressure. *N*-vinylcarbazole (NVC, TCI, >98%) was recrystallized two times from methanol. Other materials were used without further purification.

Five different chain transfer agents (CTAs) were employed in this study, as shown in Scheme 1. Benzyl dithiobenzoate (CTA 1)[45,47] and benzyl 1-pyrrolecarbodithioate (CTA 2)[48,49] were synthesized according to the procedures reported previously. *S*-Benzyl-*O*-ethyl dithiocarbonate (CTA 3),[50−52] *O*-ethyl-*S*-(1-ethoxycarbonyl) ethyldithiocarbonate (CTA 4),[53,54] and *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 5)[50,52,55] were synthesized by the reaction of potassium ethyl xanthogenate with corresponding bromide (benzyl bromide for CTA 3, methyl 2-bromopropionate for CTA 4, and 1-bromoethylbenzene for CTA 5, respectively) according to a procedure reported in the literature. These xanthate-type CTAs were finally purified by column chromatography on silica with *n*-hexane/ethyl acetate (10/1 vol %) as the eluent.

Synthesis of *S*-Vinyl Sulfides. Three vinyl sulfide derivatives having different substituent groups, 4-chlorophenyl vinyl sulfide (CPVS), 2,4-dichlorophenyl vinyl sulfide (DCPVS), and 4-bromophenyl vinyl sulfide (BPVS) were synthesized by the reaction of 1,2-dibromoethane with corresponding thiol compounds according to a previously reported method with slight modifications.[45] In a typical experiment for the synthesis of CPVS, to a solution of 13.6 g (0.20 mol) sodium ethoxide in 80 mL of ethanol was added 4-chlorobenzenethiol (28.9 g, 0.20 mol) under nitrogen. After stirring at room temperature for additional 30 min, the resulting 4-chlorobenzenethiolate was added to a solution of 56.4 g (0.30 mol) of 1,2-dibromoethane in 20 mL of ethanol at 0 °C within 1 h. Stirring was continued for 1 h, and a solution of 34.0 g (0.50 mol) of sodium ethoxide in ethanol was added. The reaction mixture was stirred at reflux for 8 h, cooled, and treated with 300 mL of benzene and 300 mL of water. The organic layer was separated, washed with water and saturated aqueous NaCl solution, and dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo*, and the residue was distilled under reduced pressure to give pure CPVS as a transparent liquid (14.7 g, 51%).

CPVS: Yield = 51%, bp 90−92 °C/0.05 mmHg (lit.[25] 91 °C/5 mmHg). ^1H NMR ($CDCl_3$): δ 7.4−7.2 (m, 4H, ArH), 6.5 (dd, 1H, $CH_2{=}CH-$), 5.4−5.3 (dd, 2H, $CH_2{=}CH-$) ppm. ^{13}C NMR ($CDCl_3$): δ 133.3, 133.0, 132.0 (ArC), 131.6 (CH═), 129.5 (ArC), 116.7 (CH_2═) ppm. Anal. Calcd for C_8H_7ClS: C, 56.30; H, 4.13; Cl, 20.77; S, 18.79. Found: C, 56.24; H, 4.29; S, 18.65.

DCPVS: Yield = 50%. bp 95−97 °C at 0.05 mmHg. ^1H NMR ($CDCl_3$): δ 7.4−7.2 (m, 3H, ArH), 6.5−6.4 (dd, 1H, $CH_2{=}CH-$), 5.6−5.5 (dd, 2H, $CH_2{=}CH-$) ppm. ^{13}C NMR ($CDCl_3$): δ 134.5, 133.2, 133.1 (ArC), 131.0 (CH═), 130.0, 129.0, 127.8 (ArC), 119.7 (CH_2═) ppm. Anal. Calcd for $C_8H_6Cl_2S$: C, 46.85; H, 2.95; Cl, 34.57; S, 15.63. Found: C, 46.55; H, 3.25 ; S, 15.87 .

BPVS: Yield = 60%. bp 85−95 °C at 0.05 mmHg (lit.[25] 110 °C/7 mmHg). ^1H NMR ($CDCl_3$): δ 7.2−7.4 (m, 4H, ArH), 6.5 (dd, 1H, $CH_2{=}CH-$), 5.3−5.4 (dd, 2H, $CH_2{=}CH-$) ppm. ^{13}C NMR ($CDCl_3$): δ 133.7, 132.3, 131.9 (ArC), 131.2 (CH═), 121.2 (ArC), 116.7 (CH_2═) ppm. Anal. Calcd for C_8H_7BrS: C, 44.67; H, 3.28; Br, 37.15; S, 14.91. Found: C, 44.20; H, 3.20; S, 15.06.

^1H and ^{13}C NMR spectra and the solubility of these monomers are shown in Figures S1 and S2 and Table S1, respectively (see Supporting Information)

General Polymerization Procedure. All polymerizations were carried out in a degassed sealed tube. A representative example is as follows:

PVS (0.27 g, 2.0 mmol), CTA 4 (4.4 mg, 0.02 mmol), and AIBN (1.6 mg, 0.01 mmol) were placed in a dry glass ampule equipped with a magnetic stir bar, and then the solution was degassed by three freeze−evacuate−thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 24 h. Since the reaction was performed in bulk, the content of the flask was gradually changed from the transparent 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 ^1H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in $CDCl_3$ at room temperature. The integration of the methine protons of the main chain in polymer (1H) at 3.4−4.2 ppm was compared with the monomer $CH_2{=}CH$-resonance (1H) at around 6.6 ppm. Conversion determined by this method was 71%. 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 (0.17 g, 64%). The resulting poly(PVS) was soluble in acetone, THF, 1,4-dioxane, ethyl acetate, chloroform, DMF, and DMSO, and insoluble in *n*-hexane, methanol, and water.

Similarly, poly(CPVS), poly(DCPVS), and poly(BPVS) were prepared by RAFT polymerization of the corresponding *S*-vinyl sulfide derivatives (CPVS, DCPVS, and BPVS). The ^1H and ^{13}C 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:

$$M_n(\text{theory}) = \frac{[\text{monomer}]_0}{[\text{CTA}]_0} \times M_{\text{monomer}} \times \text{convn} + M_{\text{CTA}} \quad (1)$$

where M_{CTA} and $M_{monomer}$ are the molecular weights of CTA and monomer, and $[\text{monomer}]_0$ and $[\text{CTA}]_0$ are the initial concentrations of monomer and CTA, respectively.

Synthesis of Block Copolymers. A representative example of the synthesis of the block copolymer composed of PVS and NVC is as follows: PVS (2.72 g, 20 mmol), CTA 4 (44.4 mg, 0.20 mmol), and AIBN (16.0 mg, 0.10 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 24 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(PVS) as a white solid (1.66 g, 61%, $M_{n,NMR}$ = 7 800 g/mol, M_w/M_n = 1.45), which was employed as a macro-CTA. The xanthate-terminated poly(PVS) (0.16 g, 0.020 mmol), AIBN (1.6 mg, 0.010 mmol), NVC (0.39 g, 2.00 mmol), and 1,4-dioxane (1.0 mL) were placed in a dry ampule. After the solution was degassed by three freeze−evacuate−thaw cycles, the polymerization was conducted at 60 °C for 24 h. The reaction mixture was purified by reprecipitation from a chloroform solution into a large excess of *n*-hexane and isolated by filtration to give a block copolymer, poly(PVS)-*b*-poly(NVC), as a white solid. The block copolymer was soluble in THF, chloroform, DMF, and insoluble in diethyl ether, *n*-hexane, methanol, and water. The copolymer composition was determined using elementary analysis by nitrogen content of the block copolymers.

Postmodifications of Poly(BPVS). Postmodifications of poly(BPVS) were conducted by a Suzuki coupling reaction according to a previously reported procedure with slight modifications.[46] The THF solution (5 mL) of poly(BPVS) (0.050 g, 0.23 unit mmol based on the repeating unit), 9-anthraceneboronic acid (0.23 g, 1.05 mmol), and tetrakis(triphenylphosphine) palladium(0) (16.1 mg, 0.014 mmol) was stirred at room temperature under nitrogen. After the mixture was completely dissolved, aqueous Na_2CO_3 solution (20 wt % in water, 0.38 mL) was added, and the reaction mixture was refluxed for 48 h in the dark. After the reaction, it was purified by reprecipitation into a large excess of methanol, and the resulting product was dried under vacuum at room temperature to give poly(BPVS-An) as a yellow solid (0.072 g, >99%). ^1H NMR ($CDCl_3$): δ 8.4−6.5 (13H, ArH), 4.6−3.3 (1H, $-CH$-S), 2.5−1.0 (2H, CH_2-CH−) ppm.

The Suzuki coupling reaction was also employed for the incorporation of the fluorene unit using 9,9-dimethylfluoren-2-boronic acid. Under the same procedure, poly(BPVS-Flu) was obtained as a beige solid (>99%). ^1H NMR ($CDCl_3$): δ 7.9−6.7 (br, 11H, ArH), 4.4−3.3 (br, 1H, $-CH-$S), 2.4−0.9 (m, 8H, CH_2−CH−, $-CH_3$) ppm.

Postmodifications of poly(BPVS) were conducted by the Buchwald−Hartwig coupling reaction according to a previously reported procedure with slight modifications.[47−49] A typical reaction procedure is as follows. Poly(BPVS) (0.050 g, 0.23 unit mmol based on the repeating unit), phenothiazine (1.22 g, 6.12 mmol), sodium *tert*-butoxide (NaO-*t*-Bu, 0.29 g, 3.06 mmol), and $Pd_2(dba)_3$ (0.047 g, 0.051 mmol) were placed in a 100 mL flask under nitrogen. Then, 1,4-dioxane (25 mL) and tri-*tert*-butylphosphine (P(*t*-Bu)$_3$, 62 mg, 0.31 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was quenched by the addition of aqueous ammonia (100 mL), and the product was extracted three times with $CHCl_3$. The product was purified by two times reprecipitation into diethyl ether. The resulting product was finally dried under vacuum at room temperature to give poly(BPVS-PTZ) as a brownish gray solid (0.077 g, >99%). ^{1}H NMR (CDCl$_3$): δ 7.9−5.9 (m, 12H, ArH), 4.3−3.1 (br, 1H, −C*H*−S), 2.3−0.9 (m, 2H, C*H*$_2$−CH−) ppm.

Similarly, the palladium-catalyzed reaction of diphenylamine into the bromophenyl moieties in poly(BPVS) afforded poly(BPVS-DPA) as a brown solid (0.066 g, 94%). ^{1}H NMR (CDCl$_3$): δ 7.7−6.6 (m, 14H, ArH), 4.2−3.0 (m, 1H, −C*H*−S), 2.4−1.0 (m, 2H, C*H*$_2$−CH−) ppm. These resulting polymers were soluble in chloroform and THF, while insoluble in acetone, diethyl ether, methanol, *n*-hexane, and water (Table S2, Supporting Information).

Instrumentation. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JEOL JNM-ECX400. Elemental analysis was carried out on a Perkin-Elmer 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): α-M (13 μm, > 1 × 10^7), α-4000 (10 μm, 4 × 10^5), α-3000 (7 μm, 9 × 10^4), α-2500 (7 μm, 5 × 10^3), 30 cm each] and a guard column [TSK-guardcolumn α, 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 1090000 were employed for calibration. The UV−vis spectra were recorded using a JASCO V-630BIO UV−vis spectrophotometer. The fluorescence spectra were obtained from a JASCO FP-6100 spectrofluorophotometer. Thermogravimetric analysis (TGA) was performed on a SEIKO TGA/6200 at a heating rate of 10 °C/min under nitrogen atmosphere.

■ RESULTS AND DISCUSSION

RAFT Polymerization of *S*-Vinyl Sulfide Derivatives. In this study, RAFT polymerization reactions of four *S*-vinyl sulfide derivatives having different substituent groups were investigated, in order to understand the polymerization mechanism of this class of monomers. When selecting RAFT agents for the polymerization of PVS, one must carefully consider the characteristic of the propagating PVS radical; accordingly, we initially studied the effect of the nature of the CTA on the radical polymerization of PVS in the presence of AIBN as an initiator (Scheme 1). Dithiocarbonates (xanthates) are known to be useful for controlling the radical polymerization of nonconjugated *O*-vinyl and *N*-vinyl monomers, such as vinyl acetate,[50−52] *N*-vinylpyrrolidone,[52−56] *N*-vinylcarbazole (NVC),[39,57,58] *N*-vinylindole,[40] and *N*-vinylphthalimide.[43] Recently, we also reported that a xanthate-type CTA was the most efficient for the synthesis of well-defined polymers by RAFT polymerization of vinyl sulfonate esters,[59,60] which can be regarded as *S*-vinyl monomers with direct linkage of the sulfonate moiety to the vinyl group. In this study, three xanthate-type mediating agents having different leaving groups (R-groups), *S*-benzyl-*O*-ethyl dithiocarbonate (CTA 3), *O*-ethyl-*S*-(1-ethoxycarbonyl) ethyldithiocarbonate (CTA 4), *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 5), were selected as CTAs. For comparison, we also employed dithiocarbamate-type (CTA 2) and dithiobenzoate-type (CTA 1) as mediating agents. Dithiobenzoate-type CTA (CTA 1) has been used for RAFT polymerization of conventional conjugated monomers, such as styrene, methyl acrylate, and *N*-isopropylacrylamide.[61−64] Dithiocarbamate-type CTA 2, in which a nitrogen lone pair is part of an aromatic ring system, has been employed for RAFT polymerizations of conventional conjugated monomers such as styrene,[35,65,66] methyl acrylate,[66] and *N*-isopropylacrylamide,[67] as well as less active monomers including *N*-vinylphthalimide[43] and *N*-vinylnaphthalimide.[68]

The bulk polymerization of PVS was conducted with different CTAs and AIBN as an initiator at 60 °C for 24 h at [M]$_0$/[CTA]$_0$ = 100, using the ratio of AIBN to CTA of 1:2 ([M]$_0$/[CTA]$_0$/[AIBN]$_0$ = 200/2/1). The results are summarized in Table 1. When the polymerization was carried out using the xanthate-type CTA 4, a poly(PVS) having a relatively low polydispersity (M_w/M_n = 1.44) was obtained with a relatively high conversion (71%, as determined by ^{1}H NMR spectroscopy). A unimodal SEC peak is detected in the SEC profiles of the poly(PVS) obtained with CTA 4; analysis of the resulting poly(PVS) via polymerization with the dithiocarbamate-type CTA 2 showed a broad unimodal SEC peak (M_w/M_n = 1.64). RAFT polymerizations of PVS with CTA 3 and CTA 5 afforded poly(PVS)s having broad molecular weight distributions (M_w/M_n = 2.29 and 1.60, respectively). Extremely low monomer conversion (<5%) was obtained for the polymerization with CTA 1 under the same conditions. These results suggest that the xanthate-type CTA 4 is effective for RAFT polymerizations of PVS, and unfavorable chain transfer and termination reactions due to the high reactivity of the propagating radicals derived from PVS could be suppressed by the RAFT process using the xanthate-type CTA. Among xanthate-type CTAs, CTA 4 showed a good balance between the leaving ability and reinitiation ability from the electron-withdrawing ester moiety that is stabilized by resonance effect. These results also support our strategy for RAFT polymerization utilizing *O*-alkyl xanthates as CTAs as a very efficient method to control the polymerization of highly reactive propagating radicals derived from PVS, even in the presence of a sulfur atom connected directly to the vinyl group of the *S*-vinyl monomer.

Table 1. RAFT Polymerization of PVS with AIBN Using Different CTAs in Bulk at 60 °C for 24 h[a]

entry	CTA[b]	convn[c] (%)	M_n[d] (theory)	M_n[e] (SEC)	M_w/M_n[e] (SEC)
1	–	77	–	18 400	2.03
2	CTA 1	<5	–	–	–
3	CTA 2	60	8400	3700	1.64
4	CTA 3	63	8800	3600	2.29
5	CTA 4	71	9900	5200	1.44
6	CTA 5	56	7900	4700	1.60

[a] [PVS]$_0$/[CTA]$_0$/[AIBN]$_0$ = 200/2/1. [b] CTA 1 = benzyl dithiobenzoete, CTA 2 = benzyl 1-pyrrolecarbodithioate, CTA 3 = *S*-benzyl-*O*-ethyl dithiocarbonate, CTA 4 = *O*-ethyl-*S*-(ethoxy carbonyl) ethyldithiocarbonate, and CTA 5 = *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate. [c] Calculated by ^{1}H NMR in CDCl$_3$. [d] The theoretical molecular weight ($M_{n,theory}$) = (MW of PVS) × [PVS]$_0$/[CTA]$_0$ × convn + (MW of CTA). [e] Measured by SEC using polystyrene standards in DMF (10 mM LiBr).

In the next stage, we examined the influence of CTA, solvent, and the [CTA]$_0$/[AIBN]$_0$ ratios in terms of monomer conversion, molecular weights, and polydispersity of the resulting poly(PVS)s. The RAFT polymerization of PVS was examined with CTA 4 at 60 °C for 24 h. The [CTA 4]$_0$/[AIBN]$_0$ ratio was adjusted between 2 and 10, while the monomer/CTA molar ratio was held constant at 100/1 (Table S3 and Figure S5, Supporting Information). When the polymerization was carried out in bulk, the monomer conversion decreased from 71% to 40% as the [CTA]$_0$/[AIBN]$_0$ ratio increased from 2 to 10, indicating a significant influence of the [CTA]$_0$/[AIBN]$_0$ ratio on monomer conversion. In contrast, the molecular weight distributions of

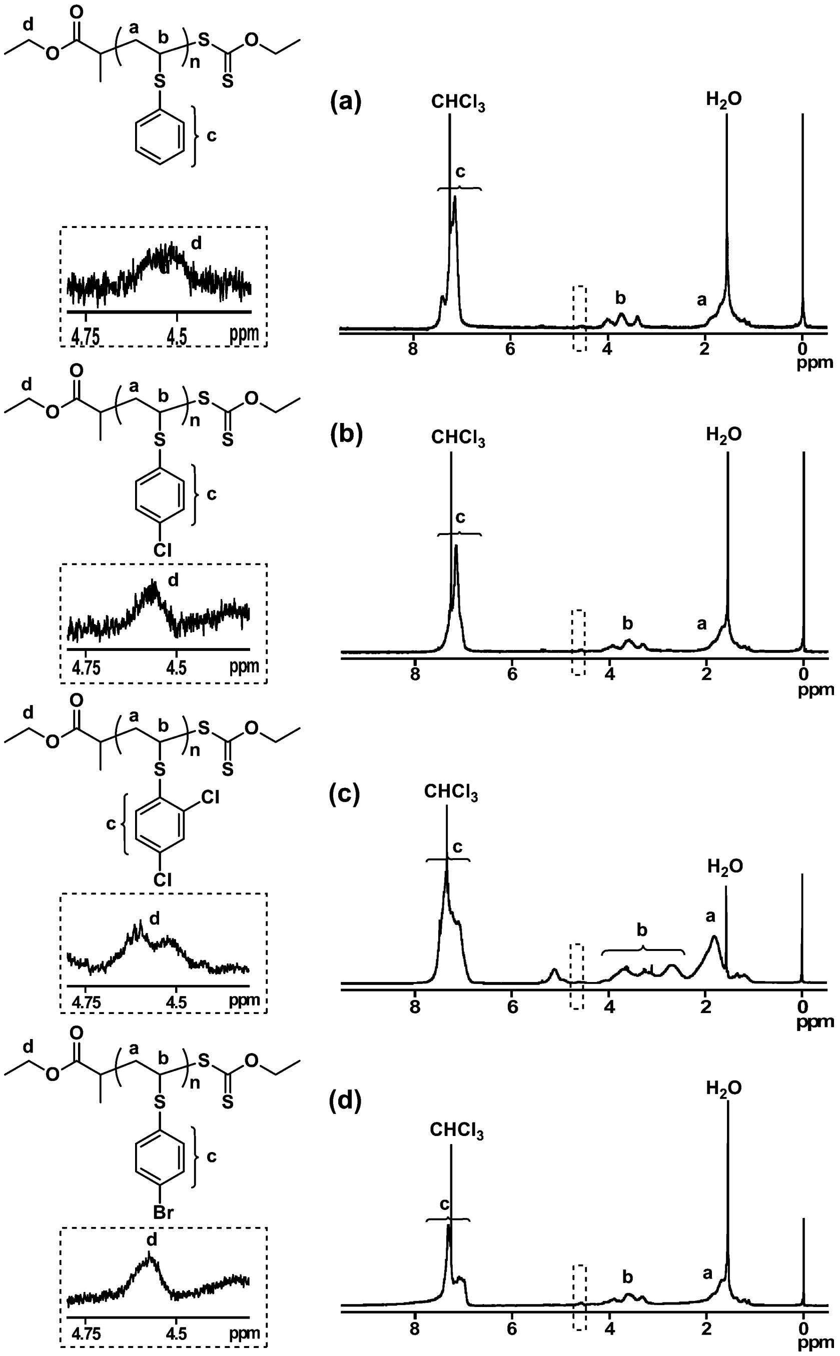


Figure 1. ^{1}H NMR spectra ($CDCl_3$) of (a) poly(PVS), (b) poly(CPVS), (c) poly(DCPVS), and (d) poly(BPVS) obtained by RAFT polymerization with CTA 4.

the resulting poly(PVS)s increased slightly with increasing the $[CTA]_0/[AIBN]_0$ ratio. This polymerization behavior is inconsistent with the general trend that higher $[CTA]_0/[AIBN]_0$ ratios (lower initiator concentration) may afford better overall control of the polymerization, as the result of a decrease in total radical species available for unfavorable side reactions. This may be due to the relatively high viscosity during the bulk polymerization of PVS; the content of the reaction mixture was actually transformed from a transparent liquid into viscous material upon reaching a certain level of conversion. Hence, the effect of the $[CTA]_0/[AIBN]_0$ ratio on the RAFT polymerization of PVS is not as remarkable.

With a view of preparing poly(PVS)s over a wide molar mass range, different degrees of polymerization were targeted. For this purpose, the polymerization of PVS was conducted at different $[M]_0/[CTA\ 4]_0$ ratios between 100 and 600, while the $[CTA]_0/[AIBN]_0$ molar ratio was held constant at 2 (see Table S4, Supporting Information). When the polymerization of PVS was conducted in bulk at 60 °C for 24 h, the number-average molecular weights of the poly(PVS)s increased from 4900 to 7500 with the $[M]_0/[CTA]_0$ ratio. A shift in the SEC trace toward higher molecular weight regions with a unimodal peak was seen with increasing $[M]_0/[CTA]_0$ ratio (Figure S6, Supporting Information), demonstrating the effective control of the molecular weights. Yet, the molecular weight distributions tend to broaden slightly with increasing $[M]_0/[CTA]_0$ ratio. This behavior can also be ascribed to the relatively high viscosity during the bulk polymerization of PVS. Nevertheless, the obtained results suggest that the molecular weights of poly(PVS)s can be easily adjusted by the monomer-to-CTA ratio, and polymers having relatively low polydispersities can be easily obtained by RAFT polymerization of PVS under suitable conditions.

In all cases, the experimental molecular weights determined by conventional SEC in DMF were found to be lower than the theoretical values. These discrepancies are believed to result from the difference in hydrodynamic volume between poly(PVS)s and the linear polystyrene standards used for SEC calibration. In order to clarify this point, NMR spectroscopy was used to determine the chain-end structure and absolute molecular weights of poly(PVS)s. The CTA-derived initiator may produce a polymer with CTA fragments at the polymer chain ends (α-chain end with the (1-ethoxycarbonyl) ethyl group and ω-chain end with the dithiocarbonate group in the case of CTA 4); the ^{1}H NMR spectrum of the poly(PVS) obtained with CTA 4 is presented in Figure 1a. The characteristic peaks at 7.6−7.1 (aromatic ring), 4.1−3.3 (CH in the polymer main chain), and 2.1−1.0 (CH_2 in the polymer main chain) ppm are clearly seen, which are attributed to the poly(PVS) main chain. In addition to these peaks, methylene protons are clearly visible at 4.7−4.4 ppm, which correspond to the two methylene protons of the end groups. This is an indication that the polymer chain end is capped with the fragments of CTA as expected according to the general mechanism of the RAFT process. The molecular weight of the polymer chain can be calculated by comparing the integrals of the peaks for the chain-end protons to those of the main-chain protons; thus, the molecular weight of poly(PVS) prepared with CTA 4 could be calculated by comparison of the area of the peaks at 4.1−3.3 ppm corresponding to the main chain protons (1H) with the peak at 4.7−4.4 ppm corresponding to the end group (peak "d" in Figure 1a). As shown in Table S4 (Supporting Information), the molecular weights determined by NMR were comparable to the theoretical values calculated using eq 1, which are apparently higher than those obtained from SEC in DMF (0.01 M LiBr) using polystyrene standards.

The controlled/living character of the polymerization of PVS was studied by performing kinetics investigations in the presence of CTA 4 with AIBN in bulk at 60 °C. When the reaction was conducted at $[PVS]_0/[CTA]_0/[AIBN]_0 = 200/2/1$, a relatively high conversion (71%) was reached after 24 h. An almost linear first-order kinetic plot is seen up to the conversion end point (24 h) under the conditions (Figure 2a). As shown in Figure 2b, a linear increase in the number-average molecular weights, M_n, with conversion is seen in the polymerization of PVS, with a decreasing polydispersity index observed with increasing monomer conversion: from $M_w/M_n = 1.79$ at 10% into 1.44 at 71%. The SEC traces of poly(PVS) obtained at different polymerization times illustrate the increase in molecular weight with time, as can be seen in Figure 2c. Symmetrical unimodal SEC peaks without shoulders and tailings are seen for the poly(PVS)s even at the last stages of polymerization, suggesting the absence of a termination reaction due to the combination of growing polymer chains during a longer reaction time.

An important criterion of a controlled/living character of polymerization is the successful extension of a chain from a preformed polymer chain as a macro-CTA. To investigate this point, the dithiocarbonate-terminated poly(PVS) prepared by the polymerization using CTA 4 was employed as a macro-CTA for chain extension experiments. The chain extension was performed in bulk at 60 °C for 24 h at different $[M]_0/[\text{macro-CTA}]_0$ ratios between 100 and 400, while the $[AIBN]_0/[\text{macro-CTA}]_0$ ratio was held constant at 1/2 (Scheme S3 and Table S5, Supporting Information). After chain extension was complete, the polymer was recovered by precipitation in methanol. The resulting products were analyzed by SEC in DMF (10 mM LiBr), and compared to the original macro-CTA. As can be seen in Figure S7 (Supporting Information), a clear shift in the SEC trace toward higher molecular ranges was observed with an increase of the $[PVS]_0/[\text{macro-CTA}]_0$ ratio. The SEC traces show unimodal peaks with no significant high molecular weight species and unreacted macro-CTA impurities. These results suggest that most of the chain ends of the

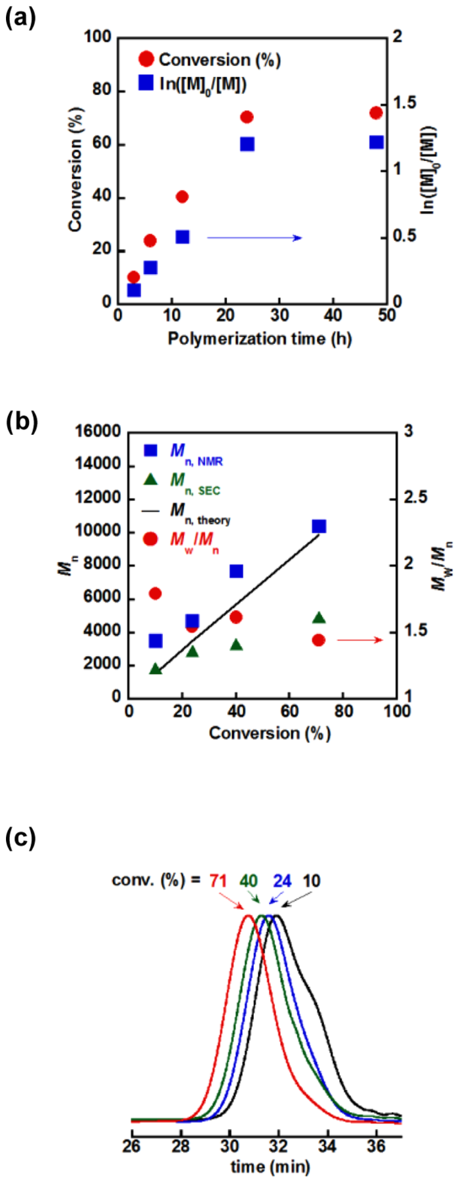


Figure 2. (a) Time−conversion (circles) and first-order kinetic (squares) plots for polymerization of PVS with AIBN in the presence of CTA 4 ($[PVS]_0/[CTA\ 4]_0/[AIBN]_0 = 200/2/1$) in bulk at 60 °C. (b) Number-average molecular weights (NMR, squares; SEC, triangles) and polydispersity (circles) as a function of conversion. (c) SEC traces of poly(PVS)s.

Table 2. RAFT Polymerization of Substituted Phenyl Vinyl Sulfides Using Different CTAs in Bulk at 60 °C for 24 h[a]

entry	monomer	CTA	convn[b] (%)	M_n[c] (theory)	M_n[b] (^{1}H NMR)	M_n[d] (SEC)	M_w/M_n[d] (SEC)
1	CPVS	–	52	–	–	14 800	1.61
2		CTA 2	50	8800	11 200	4100	1.43
3		CTA 4	53	9300	12 700	4500	1.58
4	DCPVS	–	54	–	–	7200	1.58
5		CTA 2	47	9900	10 800	3200	1.50
6		CTA 4	55	11 500	11 400	4300	1.66
7	BPVS	–	71	–	–	17 700	1.56
8		CTA 2	48	10 600	22 700	4400	1.35
9		CTA 4	59	12 900	12 200	7700	1.36

[a] $[\text{monomer}]_0/[\text{CTA}]_0/[\text{AIBN}]_0 = 200/2/1$. [b] Calculated by ^{1}H NMR in $CDCl_3$. [c] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of monomer) × $[\text{monomer}]_0/[\text{CTA}]_0$ × convn + (MW of CTA). [d] Measured by SEC using polystyrene standards in DMF (10 mM LiBr).

poly(PVS) are functionalized with the dithiocarbonate end groups, which can be used as a macro-CTA for further chain extension reactions.

The RAFT polymerization of three PVS derivatives having halogen substituted groups was also conducted at the ratio $[M]_0/[CTA]_0/[AIBN]_0 = 200/2/1$ in bulk, and the results are summarized in Table 2. When the polymerization of BPVS was carried out with the xanthate-type CTA 4 and AIBN at 60 °C for 24h, the poly(BPVS) having a relatively low polydispersity (M_w/M_n = 1.36) was obtained with a reasonable molecular weight and monomer conversion ($M_{n,NMR}$ = 12200, $M_{n,SEC}$ = 7700, convn = 59%). The polymerization of BPVS with the dithiocarbamate-type CTA 2 also afforded the bromide-substituted polymer with relatively narrow molecular weight distribution; the theoretical molecular weight, however, was inconsistent with the experimental values determined by NMR and SEC. In the cases of RAFT polymerizations of DCPVS and CPVS under the same conditions, polymers having broader polydispersities (1.43–1.66) were obtained, regardless of the nature of CTA.

The polymerization of BPVS was kinetically investigated in bulk at 60 °C and $[BPVS]_0/[CTA\ 4]_0/[I]_0 = 200/2/1$. The time–conversion and the pseudo first-order kinetic plots are shown in Figure 3a. More than 55% conversion is reached after 24 h with a curved semilogarithmic plot observed, which may be due relatively high viscosity during the bulk polymerization. A similar conversion "plateau" was also detected for RAFT polymerization of the nonsubstituted PVS. Nevertheless, a linear relationship between M_n and conversion with maintaining relatively low polydispersity is observed, as shown in Figure 3b, suggesting negligible irreversible transfer reactions. Symmetrical unimodal SEC peaks were observed for the polymers obtained even at higher conversions (>55%, Figure 3c), and the polydispersity indices for all samples ranged between 1.36 and 1.49. These results suggest that the polymerization of BPVS mediated by CTA 4 proceeds in a controlled manner at 60 °C under the conditions used in this study, even in the presence of bromine substituted group.

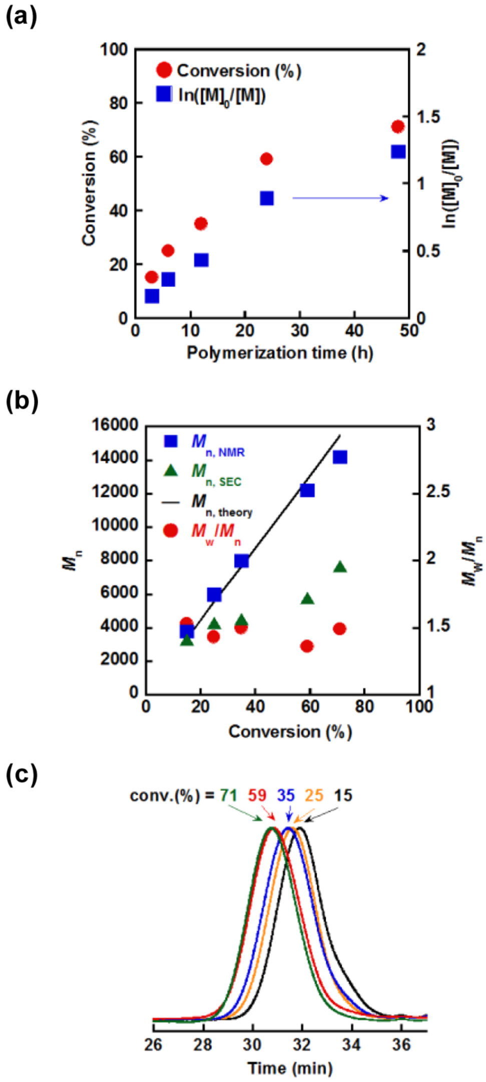


Figure 3. (a) Time–conversion (circles) and first-order kinetic (squares) plots for polymerization of BPVS with AIBN in the presence of CTA 4 in bulk at 60 °C ($[BPVS]_0/[CTA\ 4]_0/[AIBN]_0 = 200/2/1$). (b) Number-average molecular weights (NMR, squares; SEC, triangles) and polydispersity (circles) as a function of conversion. (c) SEC traces of poly(BPVS)s.

Synthesis of Block Copolymers. Block copolymers incorporating semiconducting segments and characteristic optoelectronic functions have attracted significant research interest,[69−74] because of their ability to form a variety of ordered structures via self-assembly processes and their possible applications for organic light-emitting devices, photovoltaics, and organic field-effect transistors. In particular, there is growing interest in developing novel block copolymers having two distinct electronic functionalities, such as donor and acceptor chromophores.[71,75] In this study, we selected poly(*N*-vinyl carbazole), poly(NVC), as a hydrophobic segment for the synthesis of sulfur-containing block copolymers, due to their attractive features such as hole-transporting, high charge-carrier, and electroluminescent properties.[76] Initially, we conducted the

Table 3. Synthesis of Block Copolymers by RAFT Polymerization of NVC Using Poly(*S*-vinyl sulfide) Macro-CTA at 60 °C for 24 h in 1,4-Dioxane

entry	macro-CTA	$[NVC]_0/[macro\text{-}CTA]_0$[a]	yield[b] (%)	M_n[c] (theory)	M_n[d] (EA)	M_n[e] (SEC)	M_w/M_n[e] (SEC)	composition[d] *n*:*m*
1	poly(PVS)	100	92	25 600	20 500	14 600	1.39	35:65
2		200	91	43 000	37 100	21 000	1.61	23:73
3		400	88	75 800	50 500	27 700	1.60	18:92
4	poly(BPVS)	50	83	20 200	19 400	13 200	1.24	61:39
5		100	81	27 900	28 100	19 400	1.28	41:59
6		200	92	47 800	47 000	28 500	1.36	24:76
7		400	98	89 500	99 900	40 600	1.54	11:89

[a] $[macro\text{-}CTA]_0/[AIBN]_0 = 2$, [M] = 0.464 g/mL, Macro-CTA = poly(PVS): $M_{n,\ NMR}$ =7,800, $M_{n,\ SEC}$ = 4,900, M_w/M_n = 1.45, poly(BPVS): $M_{n,\ NMR}$ = 12,200, $M_{n,\ SEC}$ = 7,700, M_w/M_n = 1.36. [b] Hexane-insoluble part. [c] The theoretical molecular weight ($M_{n,theory}$) = (MW of NVC) × $[NVC]_0/[Macro\text{-}CTA]_0$ × yield + (MW of Macro-CTA). [d] Calculated by elemental analysis (EA). [e] Measured by SEC using polystyrene standards in DMF (10 mM LiBr).

synthesis of a block copolymer by RAFT polymerization of NVC using poly(PVS) as a macro-CTA, as shown in Scheme 2a. For the synthesis of well-defined block copolymers by the RAFT process, the order of blocking is crucial. In this case, the first xanthate-terminated poly(PVS) should have a high transfer constant in the subsequent polymerization of the second NVC monomer, to give the second block.[77,78] Additionally, in order to achieve block copolymer with low polydispersity, the rapid conversion of macro-CTA to block copolymer is also required, by which all of the second blocks can be initiated approximately at the same time. It should be noted that RAFT agents suitable for controlling the polymerization of nonconjugated monomers (less activated monomers including *O*-vinyl and *N*-vinyl monomers) tend to be ineffective with conjugated monomers (more activated monomers including styrene and (meth)-acrylates).[79] Since the resonance stabilization of propagating radicals derived from PVS ($Q = 0.32$, $e = -1.4$) is slightly higher than that of NVC ($Q = 0.26$, $e = -1.29$), it is reasonable to expect that the leaving ability of the propagating poly(PVS) radical is higher than that of the second poly(NVC) radical, in addition to the steric hindrance impaired by the macro-CTA.

The xanthate-terminated poly(PVS) having low molecular weight was initially prepared by RAFT polymerization with CTA 4. The polymerization of NVC was conducted in the presence of the xanthate-terminated poly(PVS) as a macro-CTA in dry 1,4-dioxane at 60 °C for 24 h, while maintaining the $[macro\text{-}CTA]_0/[AIBN]_0$ ratio at a constant value of 2:1. The $[NVC]_0/[macro\text{-}CTA]_0$ ratio was varied from 100 to 400 to control the comonomer content and molecular weight. The reaction conditions, monomer conversion, molecular weights, polydispersities, and comonomer compositions are summarized in Table 3. Figure 4a shows the SEC traces of the parent poly(PVS) and resulting block products. The SEC chromatograms of the starting macro-CTA and the growth polymers show a clear shift of the molecular weight to the higher molecular ranges. A slight tailing can be seen in the SEC traces of the block copolymers, which could be due to some RAFT *Z*-group loss in the macro-CTA. Nevertheless, the block copolymers, poly(PVS)-*b*-poly(NVC)s, having relatively higher molecular weights ($M_{n,EA}$ = 20 500−50 500, M_w/M_n = 1.39−1.61) were obtained with reasonable conversion (yield = 88−92%). The ^1H NMR spectrum of the block copolymer, poly(PVS)-*b*-poly(NVC), is shown in Figure 5a. The peaks corresponding to poly(NVC) and poly(PVS) are clearly observed in the spectrum measured in $CDCl_3$. These results suggest that, under the conditions employed in this study, fragmentation from the intermediate radical to the xanthate-terminated poly(PVS), as well as the reinitiation process, are sufficiently effective, resulting in the rapid conversion of the macro-CTA into the block copolymer.

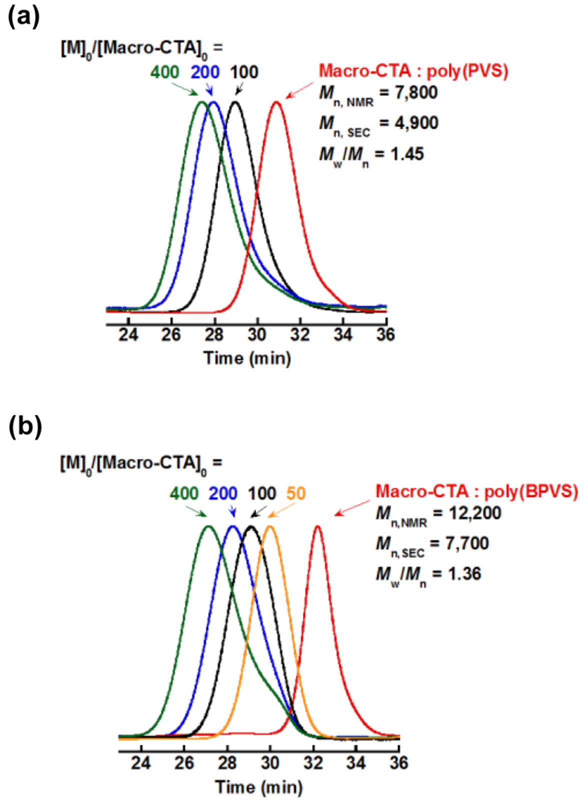


Figure 4. (a) Poly(PVS) macro-CTA (red line, $M_{n,NMR}$ = 7800, $M_{n,SEC}$ = 4900, M_w/M_n = 1.45) and the products obtained by the polymerization of NVC and (b) poly(BPVS) macro-CTA (red line, $M_{n,NMR}$ = 12 200, $M_{n,SEC}$ = 7700, M_w/M_n = 1.36) and the products obtained by the polymerization of NVC.

The synthesis of block copolymers was also conducted by RAFT polymerization of NVC using poly(BPVS) as the macro-CTA, which was initially prepared by RAFT polymerization with CTA 4. When the polymerization of NVC was conducted in dry 1,4-dioxane using the xanthate-terminated poly(BPVS) macro-CTA at $[NVC]_0/[macro\text{-}CTA]_0$ = 50−400, high monomer conversions (83−98%) were reached at 60 °C after 24 h (Table 3). As can be seen in Figure 4b, the comparison of the SEC traces of the starting macro-CTA with the corresponding block copolymers shows a clear shift to higher molecular weights for the block copolymers. The molecular

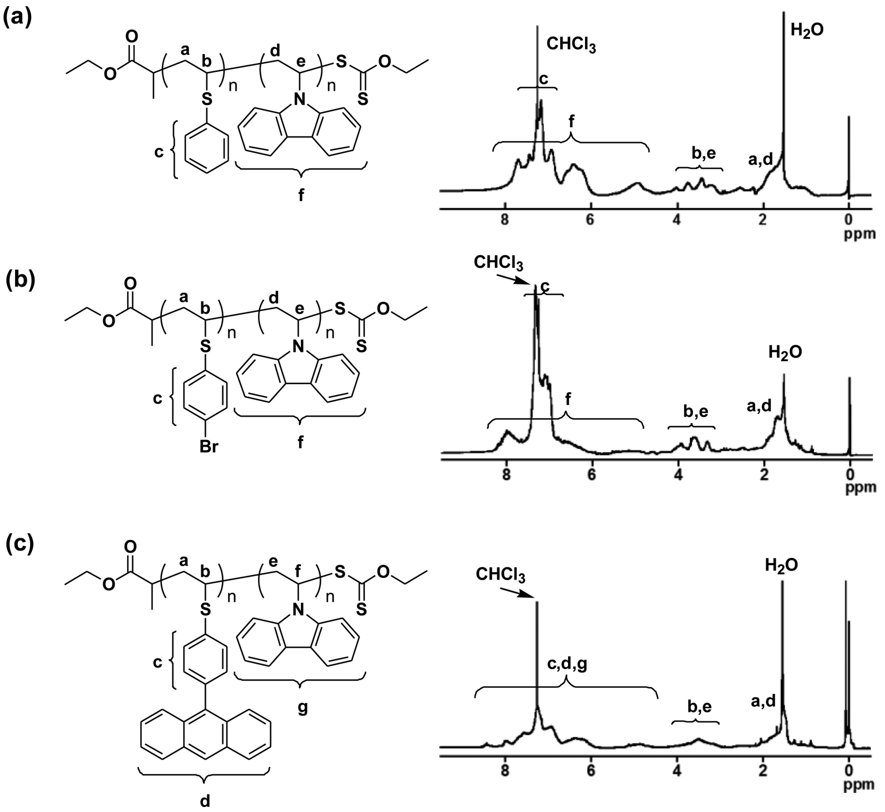


Figure 5. ^{1}H NMR spectra ($CDCl_3$) of (a) poly(PVS-*b*-NVC), (b) poly(BPVS-*b*-NVC), and (c) poly(BPVS-An-*b*-NVC).

weight distributions displayed a narrow dispersity (1.24−1.36) up to [NVC]/[macro-CTA] = 200, with unimodal SEC traces and high-molecular-weight species being absent. In the ^{1}H NMR spectrum of the block copolymer measured in $CDCl_3$, peaks corresponding to both components are clearly detected (Figure 5b). In all cases, the molecular weights of the block copolymers evaluated from the composition determined by elemental analysis and the molecular weight of the poly(BPVS) macro-CTA were comparable to the theoretical values. These results clearly demonstrate that the chain extension from the poly(BPVS) macro-CTA to NVC is a controllable process and provides block copolymer with as-designed chain structure and relatively narrow molecular weight distribution. Note that there was the tendency for the controlled polymerization to be difficult with an increase of $[NVC]_0/[\text{macro-CTA}]_0$ ratio, that is, the slight tailing in the lower molecular weight regions due to the increase in the viscosity or the byproducts formed by the unfavorable chain transfer and termination reactions was observed at [NVC]/[macro-CTA] = 400 (Figure 4b).

The RAFT polymerization of PVS with a xanthate-terminated poly(NVC), which was prepared by RAFT polymerization of NVC in the presence of CTA 4, was also conducted for the synthesis of the corresponding block copolymer (Scheme S4 and Table S6, Supporting Information). When the polymerization of PVS was conducted using the xanthate-terminated poly(NVC) in bulk at 60 °C, the polymerization was relatively slow (yield =69−33% after 24 h at $[PVS]_0/[\text{macro-CTA}]_0/[AIBN]_0$ = 800−200/2/1). As can be seen in Figure S8 (Supporting Information), a shift in the SEC trace toward a higher molecular weight region was seen after the chain extension, while the resulting products showed broad SEC traces with an apparent shoulder peak at low molecular weight regions. The results indicated the possible existence in the final product of a certain quantity of residual low-molecular-weight chains, possibly corresponding to unreacted or dead chains. That is, the leaving ability of the propagating poly(NVC) radical was lower than that of the second poly(PVS) radical in this system, resulting in insufficient block formation. A similar result was also observed for the RAFT polymerization of BPVS using the xanthate-terminated poly(NVC) as a macro-CTA (Table S7 and Figure S9, Supporting Information). Overall, we confirmed that the order of the blocks is crucial for the synthesis of well-defined block copolymers composed of poly(NVC) and poly(*S*-vinyl sulfide) derivatives; block copolymers could be obtained by RAFT polymerization of NVC using poly(*S*-vinyl sulfide) macro-CTA, whereas polymerization with an opposite order afforded insufficient products.

Very recently, Keddie and Moad reported that controlled character of the RAFT polymerization of NVC was achieved using trithiocarbonates, allowing for the synthesis of homopolymers and block copolymers with low polydispersities.[80] Hence, we evaluated RAFT polymerization of *S*-vinyl sulfide monomer using trithiocarbonates. Our preliminary experiments indicated that the controlled character of the polymerization of PVS with trithiocarbonates were comparable to that with xanthate-type CTAs used in this study (Figure S10, Supporting Information), suggesting that trithiocarbonate-type CTAs also have a potential for the controlled synthesis of block copolymers. Experiments aiming to synthesize various block copolymers composed of conjugated monomers and nonconjugated *S*-vinyl sulfides using various CTAs are now in progress, which will be reported separately.

Postmodifications. The incorporations of photoactive chromophores on the halide units of the poly(BPVS) was conducted by postmodifications using Suzuki and Buchwald−

Table 4. Postmodifications of Poly(BPVS) with Optoelectronic Compounds

polymer	reactant[a]	catal./base	yield[b]	DS (%)[c] (^{1}H NMR (EA))	T_{d10}[d] (°C)	λ_{max}^{abs} (nm)[e]	λ_{max}^{ex} (nm)[e]
poly(BPVS)	–	–	–	–	302	266	–
poly(BPVS-An)	An	$Pd(PPh_3)_4/Na_2CO_3$[f]	>99	>99	340	369	415
poly(BPVS-Flu)	Flu		>99	>99	347	314	376
poly(BPVS-DPA)	DPA	$Pd_2(dba)_3$ /NaO-*t*-Bu[g]	94	74 (64)	332	308	377
poly(BPVS-PTZ)	PTZ		>99	>99 (94)	339	320	446

[a] An = 9-anthraceneboronic acid, Flu = 9,9-dimethylfluoren-2-boronic acid, DPA = diphenylamine, and PTZ = phenothiazine. [b] Poly(BPVS-An) and poly(BPVS-Flu): methanol-insoluble part. Poly(BPVS-DPA) and poly(BPVS-PTZ): diethyl ether insoluble part. [c] DS = degree of substitution calculated by ^{1}H NMR and elemental analysis. [d] Determined by TGA; heating rate = 10 °C/min; N_2 atmosphere. [e] Measured by THF solution. [f] Reaction was conducted in the presence of Na_2CO_3 (10 equiv for the bromo unit) and $Pd(PPh_3)_4$ (6 mol % for the bromo unit) in THF under reflux for 48 h. [g] Reaction was conducted in the presence of NaO-*t*-Bu (15 equiv for the bromo unit), $Pd_2(dba)_3$ (25 mol % for the bromo unit), and ligand (P(*t*-Bu)$_3$, P/Pd ratio = 3/1) in 1,4-dioxane at 100 °C for 24 h.

Hartwig coupling reactions, as shown in Scheme 3. An advantage of the postmodification methods is its versatility, even if postmodification reactions in polymers can suffer occasionally from lower conversion. When the optimal postmodification route which afforded the quantitative conversion was found, however the postmodification route can be a useful method for the incorporation of the various substituents. In contrast, the synthetic route with the monomer synthesis with the optoelectronic functionality, followed by the polymerization, may suffer from the low solubility and low polymerization rate of the higher molecular weight monomer. Table 4 summarizes the results of the palladium-catalyzed coupling reactions of poly(BPVS). Initially, the Suzuki-coupling reaction of poly(BPVS) using a monofunctional boronic acid was conducted with tetrakis(triphenylphosphine)palladium(0) as a catalyst under basic conditions, as shown in Scheme 3a. The poly(BPVS) obtained by RAFT polymerization was reacted with a large excess of 9-anthraceneboronic acid in the presence of the Pd catalyst and Na_2CO_3 in THF/water. Purification of the product was conducted by precipitation into methanol, yielding a yellow product, which was soluble in a number of organic solvents, including chloroform and THF (Table S2, Supporting Information). Product yield was calculated on the basis of the amount of aryl halide unit in the feed and the conversion. The ^{1}H NMR spectrum of the product shows the characteristic broad peaks at 6.5−8.5 ppm (Figure 6b), which are attributed to the phenyl and anthryl groups. Comparison of the ^{1}H NMR spectra of the resulting poly(BPVS-An) and the poly(BPVS) used as a starting polymer revealed an increase in peak intensity of the aromatic signals after the postmodification. Conversion of the coupling reaction determined by comparison of the aromatic peaks at 6.5−8.4 ppm (13H) to the peaks at 3.3−4.6 ppm attributed to the main chain (1H) was estimated to be 99%. The Suzuki-coupling reaction of poly(BPVS) using 9,9-dimethylfluoren-2-boronic acid under the same conditions afforded poly(BPVS-Flu) quantitatively, which was evaluated by ^{1}H NMR (Figure 6c).

Buchwald−Hartwig coupling reactions between the pendant bromophenyl group of poly(BPVS) with photoactive compounds having an N−H bond were conducted using tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) as a catalyst, sodium *tert*-butoxide (NaO-*t*-Bu) as a base, and tri*tert*-butylphosphine (P(*t*-Bu)$_3$) as a ligand according to procedures reported previously (Scheme 3b).[47−49] Table 4 shows the results of the Buchwald−Hartwig coupling reactions of poly(BPVS-Br) using phenothiazine and diphenylamine. The reaction of poly(BPVS) with phenothiazine was conducted in 1.4-dioxane at 100 °C for 24 h. The ^{1}H NMR spectrum of the product, poly(BPVS-PTZ), shows all characteristic proton signals corresponding to the methylene (0.9−2.3 ppm), methine main chain (3.1−4.3 ppm), and phenyl groups (5.9−7.9) ppm (Figure 6e). The conversion calculated by comparison of the signals at 3.1−4.3 ppm corresponding to the methine protons in the main chain to the signal at 5.9−7.9 ppm corresponding to the aromatic protons was estimated to be >99%, which is in fair agreement with the value determined by the elemental analysis (nitrogen content). The introduction of diphenylamine on the aryl halide unit proceeded smoothly with a relatively high conversion to afford sulfur-containing polymers with the triphenyl amine unit in the side chain (Figure 6d). In all cases, the magnification of ^{1}H NMR spectra of the products in the range of 6.0−9.5 ppm indicated clearly the incorporation of photoactive chromophores, which were quite different from that of the poly(BPVS) (Figure S11, Supporting Information). These results indicate that both the Suzuki and Buchwald−Hartwig coupling reactions are effective methods for the introduction of additional optoelectronic components into the bromophenyl unit of the poly(BPVS), producing novel sulfur-containing polymers having additional electronic functionalities with high conversions (degrees of the substitution) and recoveries.

Postmodification of the block copolymer, poly(BPVS-An-*b*-NVC), was also attempted using the Suzuki coupling reaction. Incorporation of the anthracene unit onto the poly(BPVS) segment in the block copolymer was carried out with a large excess of 9-anthraceneboronic acid in the presence of the Pd catalyst and Na_2CO_3 in THF/water under the same conditions. As can be seen in Figure 5c, the ^{1}H NMR spectrum of the resulting poly(BPVS-An-*b*-NVC) showed characteristic broad peaks at 6.5−8.4 ppm attributed to the phenyl and anthryl groups, suggesting the incorporation of the photoactive chromophore. The resulting novel block copolymer has two distinct electronic functionalities, in which the carbazole-containing segment is covalently linked with the anthracene-containing segment.

Optical and Thermal Properties. For the investigation of characteristic optoelectronic properties, we employed four polymers having different substituent groups, poly(BPVS-An), poly(BPVS-Flu), poly(BPVS-DPA), and poly(BPVS-PTZ), which were modified with anthracene, fluorene, diphenylamine, and phenothiazine, respectively. Figure 7a depicts the absorbance spectra of the poly(BPVS) and modified polymers in THF. Poly(BPVS) has a maximum absorption peak at ca. 270 nm due to the phenyl groups. After modification, the characteristic absorption peaks corresponding to the incorporated optoelectronic moieties are clearly observed at ca. 330−

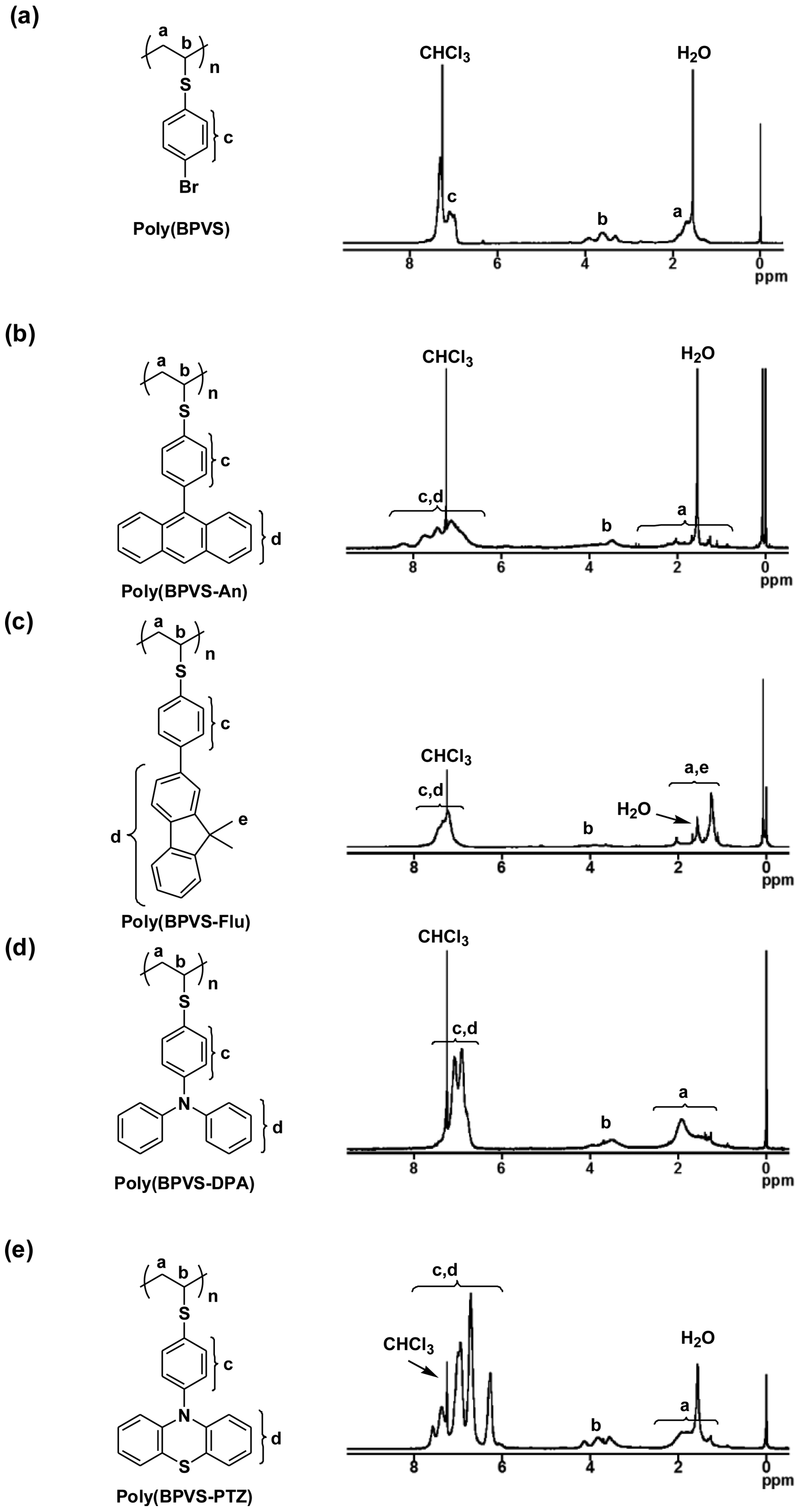


Figure 6. ^{1}H NMR spectra ($CDCl_3$) of (a) poly(BPVS) used as a starting material, and (b-e) resulting polymers obtained after postmodifications.

400, 300−350, 280−350, and 300−350 nm in poly(BPVS-An), poly(BPVS-Flu), poly(BPVS-DPA), and poly(BPVS-PTZ), respectively. The fluorescence properties of poly(BPVS), poly(BPVS-An), poly(BPVS-Flu), poly(BPVS-DPA), and poly(BPVS-PTZ) were also investigated. As can be seen in parts c and d of Figure 7, poly(BPVS) shows no fluorescence whereas the four modified polymers show the fluorescence due to the incorporation of optoelectronic moieties. Poly(BPVS-An),

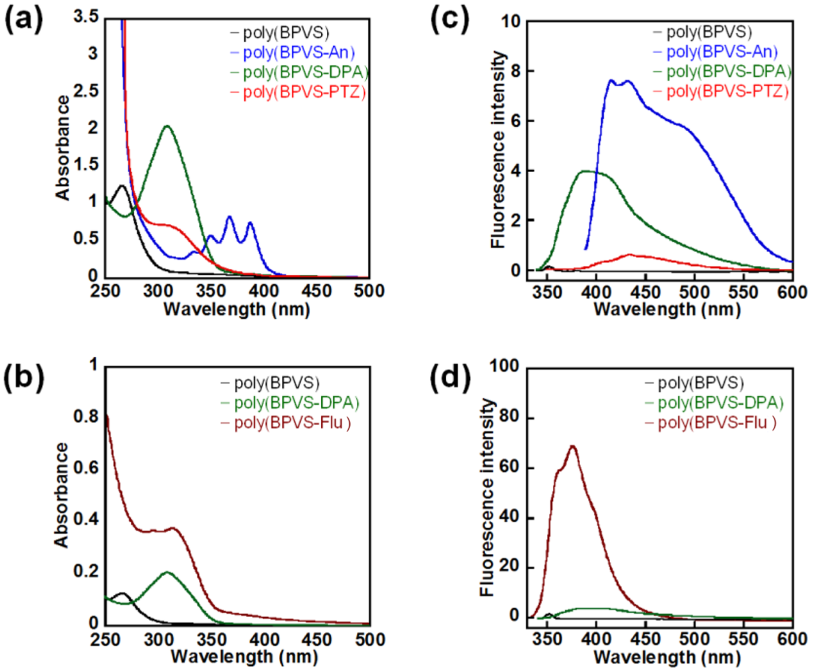


Figure 7. Absorption (concentration = (a) 1.0 × 10^{-4} chromophore unit mol/L and (b) 1.0 × 10^{-5} chromophore unit mol/L in THF) and fluorescence spectra (concentration = (c, d) 1.0 × 10^{-5} chromophore unit mol/L in THF) of the resulting polymers. Exciting wavelength: poly(BPVS), 308 nm; poly(BPVS-An), 369 nm; poly(BPVS-Flu), 314 nm; poly(BPVS-DPA), 308 nm; poly(BPVS-PTZ), 320 nm.

poly(BPVS-Flu), poly(BPVS-DPA), and poly(BPVS-PTZ) have the fluorescence in a range of ca. 400–600, 350–450, 350–550, and 370–530 nm, respectively. The strongest fluorescence is, in particular, observed in poly(BPVS-Flu), which resulted from the high quantum efficiency of the fluorene moiety.

The absorption and fluorescence properties of the block copolymers, poly(BPVS-*b*-NVC) and poly(BPVS-An-*b*-NVC) obtained by postmodification, are shown in Figure 8. The absorption due to the poly(NVC) segment is observed at ca. 300–350 nm in the parent block copolymer, poly(BPVS-*b*-NVC). After postmodification, poly(BPVS-An-*b*-NVC) shows the absorption due to the anthracene groups at ca. 350–400 nm, which indicates incorporation of the anthracene group; this result was consistent with the ^{1}H NMR analysis of poly(BPVS-An-*b*-NVC). In the thin film state, the absorption spectrum is slightly red-shifted compared to that of the THF solution state, suggesting a specific conformation in the thin film. Fluorescence spectra of poly(BPVS-*b*-NVC) shows a fluorescence at ca. 350–500 nm, which corresponds to that of the poly(NVC) segment. In the case of poly(BPVS-An-*b*-NVC), a strong fluorescence due to the anthracene groups is also observed in a range of 350–500 nm (excitation wavelength: 294 nm). The formation of an excimer (i.e., the carbazole–carbazole and anthracene–anthracene dimer, respectively) can be observed according to the previous literature;[81−83] however, fluorescence due to such excimer species was not observed in poly(BPVS-An-*b*-NVC), which is likely due to the fact that the relatively bulky side chains (i.e., 9-phenylanthracene groups) would prevent the formation of excimers. The obtained results demonstrate that the control of the fluorescence behaviors of poly(BPVS)-based homopolymer and block copolymer were successfully achieved by the incorporation of various optoelectronic groups by efficient palladium-catalyzed coupling reactions, and besides, the tuning of other properties such as the electrochemical behaviors can be expected by using this system.

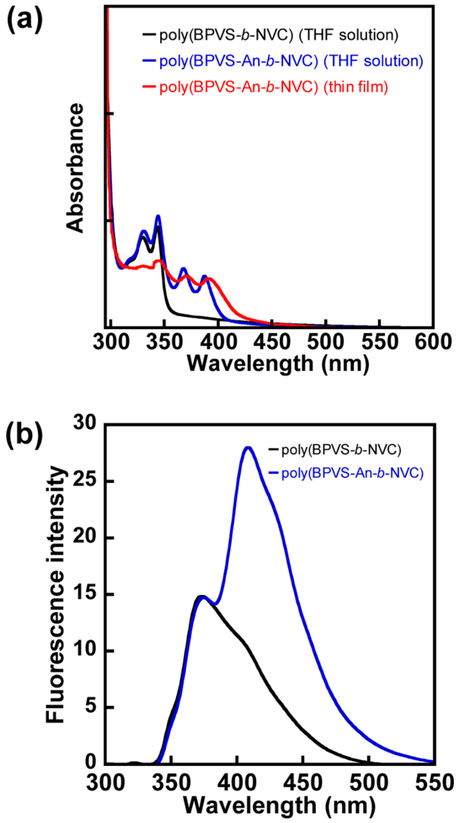


Figure 8. Absorption spectra (concentration = 1.0 × 10^{-4} chromophore unit mol/L in THF) and fluorescence spectra (concentration = 1.0 × 10^{-5} chromophore unit mol/L in THF) of the resulting block copolymers. Excited wavelength: 294 nm.

The thermal properties of the modified polymers were evaluated by TG measurements. As shown in Figure 9, the poly(BPVS) was stable up to 280 °C, and then the thermal degradation started. The temperature for the 10% weight loss of poly(BPVS-An) under a nitrogen atmosphere was 340 °C, which is notably higher than that of poly(BPVS) (T_d^{10} = 302 °C). The other modified polymers showed similar thermal stabilities with decomposition occurring above 300 °C. The 10% weight loss temperatures of poly(BPVS-Flu), poly(BPVS-DPA), and poly(BPVS-PTZ) under a nitrogen atmosphere were 347, 332, and 339 °C, respectively. These results indicated that the modified polymers exhibited high thermal stabilities, regardless of the nature of the substituent groups. Our preliminary experiment suggested that poly(PVS) had relatively high refractive index (n_D = ca. 1.62). Further studies for such directions are now in progress, which will be reported separately.

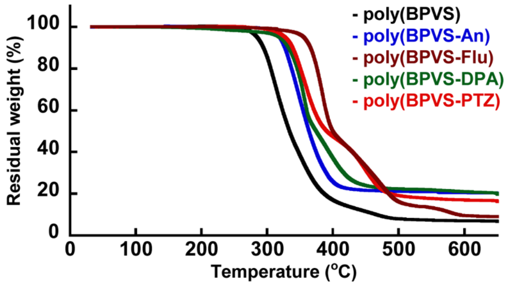


Figure 9. TGA thermograms of the polymers obtained by post-modifications of poly(BPVS).

CONCLUSION

We have demonstrated the controlled synthesis of sulfur-containing homopolymers and block copolymers by RAFT polymerization of *S*-vinyl sulfide derivatives, in which the thioether group is directly connected to the vinyl group. The xanthate-type mediating agent, CTA 4, was found to be the most effective for the controlled polymerization of the nonsubstituted PVS and BPVS. The controlled character of the polymerization of the two *S*-vinyl monomers was confirmed. Novel block copolymers based on nonconjugated *S*-vinyl and *N*-vinyl monomers were synthesized by RAFT polymerization of NVC using poly(*S*-vinyl sulfide) derivatives as a macro-CTA. We believe that this work represents the first report on the controlled radical polymerization of *S*-vinyl sulfide derivatives, and synthesis of sulfur-containing block copolymers derived from *S*-vinyl sulfides. Palladium-catalyzed coupling reactions were found to be an effective method for incorporation of additional optoelectronic components in the poly(BPVS) as well as poly(BPVS-An-*b*-NVC), affording a novel block copolymer with two distinct electronic functionalities. This work substantially broadens and extends the field of functional sulfur-containing polymers, in which the control of the molecular weight, polydispersity, topology, composition, and functions can be achieved using the controlled radical polymerization of *S*-vinyl monomers.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing ^{1}H and ^{13}C NMR spectra of the monomers and polymers, tables summarizing the solubility of the products and polymerization results under various conditions, reaction schemes, and GPC traces of the resulting polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*(H.M.) E-mail: h.mori@yz.yamagata-u.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (24350053).

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