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ARTICLE

RAFT Polymerization of Vinylthiophene Derivatives and Synthesis of Block Copolymers Having Cross-Linkable Segments

Hideharu Mori,[*,†] **Ken Takano,**[†] **and Takeshi Endo**[‡]

[†]*Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa 992-8510, Japan, and* [‡]*Molecular Engineering Institute, Kinki University, Iizuka, Fukuoka 820-8555, Japan*

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ABSTRACT: The polymerization of three vinylthiophene derivatives, 2-vinylthiophene (2VT), 3-vinylthiophene (3VT), and 2,5-dibromo-3-vinylthiophene (DB3VT), was carried out by reversible addition−fragmentation chain transfer (RAFT) process using six different chain transfer agents (CTAs). The novel doubly polymerizable monomer, DB3VT, undergoes controlled radical polymerization via the RAFT process, followed by Suzuki coupling reaction. Two dithiobenzoate-type RAFT agents, phenylethyl dithiobenzoate (CTA 2) and cumyl dithiobenzoate (CTA 3), were the most efficient to obtain poly(DB3VT) with controlled molecular weights and low polydispersities ($M_w/M_n = 1.05-1.15$). Good control of the polymerization of DB3VT was confirmed by the linear increase in the molecular weight with the conversion and the ability to extend the chain by a second addition of the monomer. Chain extension from poly(methyl methacrylate) to DB3VT could be well controlled under suitable conditions and provided block copolymers having cross-linkable poly(DB3VT) segments with as-designed chain structures and low polydispersities. The block copolymers were also synthesized by RAFT polymerization of DB3VT using poly(methyl acrylate) as a macro-chain transfer agent (macro-CTA). Modifications of the 2,5-dibromide group of poly(DB3VT) by Suzuki coupling reaction using difunctional boronic acid afforded a network material, whereas a soluble composite having an extended π-structure was obtained by the coupling reaction of the block copolymer, poly(methyl methacrylate)-*b*-poly(DB3VT).

Introduction

Poly(thiophene)s represent a class of conducting polymers that have good conductivity and chemical stability in both the natural and doped states.[1] Block copolymers incorporating polythiophenes, oligothiophenes, and their derivatives have attracted significant research interest, which is mainly due to their feasibility to create highly ordered structures as well as their potential applications in the optoelectronic fields.[2,3] Hierarchical structures of block copolymers formed via self-assembly are generally dependent on the structure of each segment, composition, and chain length, in addition to external factors, such as kind of solvent, concentration of the solution, and temperature. To manipulate unique electronic and semiconducting functions derived from the highly ordered nanostructure, the synthetic method to precisely control the molecular weight, polydispersity, topology, and composition of each block is greatly needed. Anionic polymerization of conventional vinyl monomers[4,5] was initially employed to produce block copolymers containing oligothiophenes and poly(thiophene)s. Another approach to create block copolymers is to introduce pendant conjugated oligomers to nonconjugated polymer prepared by anionic polymerization.[6] Recent development in chain growth polycondensation has also provided methodologies to synthesize well-defined poly(thiophene) derivatives having low polydispersity.[7−9] Controlled radical polymerization[10,11]and anionic polymerization[12] of vinyl monomers from functionalized chain end of the well-defined regioregular polythiophene afforded a variety of conducting block copolymers.

Several attempts to synthesize poly(vinylthiophene) derivatives have appeared in the literature. Trumbo et al. reported free radical (co)polymerizations of various vinylthiophene derivatives, such as 2-vinylthiophene (2VT),[13−16] 3-vinylthiophene (3VT),[14−17] 4-bromo-2-vinylthiophene,[18] 3-methyl-2-vinylthiophene,[19,20] 5-alkyl-2-vinylthiophene,[21−23] 5-bromo-2-vinylthiophene,[24] 5-chloro-2-vinylthiophene,[24] 5-methoxy-2-vinylthiophene,[25] and 2,5-dimethyl-3-vinylthiophene,[26,27] Cationic polymerization[28,29] and electrochemical polymerization[30,31] of 2VT were also reported. Other examples involve the polymerization of vinyl oligothiphenes,[32,33] 3′-vinyl-2,2′:5′,2″-terthiophene,[34] 5-vinyl-2,2′:5′,2″-terthiophene,[35]and *N*-phenyl-2-(2′-thienyl)-5-(5″-vinyl-2″-thienyl)pyrrole.[36] To the best of our knowledge, controlled radical polymerization of these vinyl thiophene derivatives has never been described before.

We now report the synthesis of poly(vinylthiophene) derivatives with predetermined molecular weights and narrow polydispersity by reversible addition−fragmentation chain transfer (RAFT) polymerization. In order to understand the polymerization mechanism of this class of monomers, we selected three different vinylthiophene derivatives, 2-vinylthiophene (2VT), 3-vinylthiophene (3VT), and 2,5-dibromo-3-vinylthiohene (DB3VT), as shown in Scheme 1. In particular, DB3VT is polymerizable via RAFT polymerization of vinyl group and potentially through a dehalogenation polycondensation through the brominated thienyl group. In the first part, we briefly compare the polymerization behavior of three vinylthiophene derivatives. Then, we describe RAFT polymerization of the novel doubly polymerizable monomer, DB3VT, using suitable chain transfer agents (CTAs) and polymerization conditions and the synthesis of well-defined block copolymers having a cross-linkable poly(DB3VT) segment.

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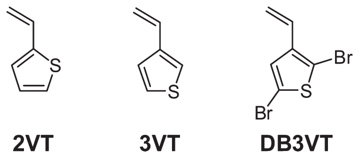
*To whom correspondence should be addressed: E-mail h.mori@yz.yamagata-u.ac.jp; Ph +81-238-26-3765; Fax +81-238-26-3749.

Scheme 1. Structures of Vinylthiophene Derivatives



Finally, the modification of the 2,5-dibromide group of poly(DB3VT) by Suzuki coupling reaction was investigated. Selective Suzuki coupling reaction of the homopolymer using a monofunctional boronic acid led to the formation of poly(vinylterthiophene), whereas a difunctional boronic acid could be used as a cross-linking agent to afford a network material. Modifications of the 2,5-dibromide group in the block copolymer, poly(methyl methacrylate)-*b*-poly(DB3VT), using difunctional boronic acid yielded a soluble composite having an extended π-structure.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. 1,4-Dioxane (Kanto Chemical, 99%) and tetrahydrofuran (THF, Kanto Chemical, 99.5%) were distilled from sodium wire. Note that distilled dioxane was stored under a nitrogen atmosphere in the dark, which was carefully employed for the polymerization, because of the possible effect of peroxide impurities in the solvent.[37] 3-Thiophenecarboxaldehyde (Aldrich Chemical, 98%) was purified by column chromatography on silica with *n*-hexane/ethyl acetate (2/1) as the eluent, followed by vacuum distillation. 2-Thiophenecarboxaldehyde (Tokyo Kasei Kogyo, 97%) was purified by distillation. Methyltriphenylphosphonium bromide (ACROS, 98%), bromine (Kanto Chemical, 99%), sodium hydrogen carbonate (Kanto Chemical, 99%), and *n*-butyllithium (Kanto Chemical, 2.6 M *n*-hexane solution) were used as received. Methyl acrylate (MA, Tokyo Kasei Kogyo, 98%) and methyl methacrylate (MMA, Kanto Chemical, Cica reagent) were distilled in vacuo. Other materials were used without further purification.

Synthesis of Chain Transfer Agents (CTA)s. Six different CTAs were employed in this study, as shown in Scheme 2. Benzyl dithiobenzoate (CTA 1) was synthesized by the reaction of a carbodithioate salt with an alkylating agent according to the procedure reported previously.[38,39] CTA 1 was purified by vacuum distillation using a glass tube oven (Shibata GTO-250RS) to give a red oil. 1-Phenylethyl dithiobenzoate (CTA 2) and cumyl dithiobenzoate (CTA 3) were prepared according to literature procedures.[40,41] Both CTAs were finally purified by column chromatography on silica with *n*-hexane as the eluent. Benzyl 1-pyrrolecarbodithioate (CTA 4) was synthesized according to the procedure reported previously.[42,43] CTA 4 was finally purified by column chromatography on silica with *n*-hexane/ethyl acetate (10/1 vol %) as the eluent. *S*-Benzyl-*O*-ethyl dithiocarbonate (CTA 5) and *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 6) were synthesized by the reaction of potassium ethyl xanthogenate and the corresponding bromide (benzyl bromide for CTA 5 and 1-bromoethylbenzene for CTA 6) in ethanol according to a procedure reported in the literature.[44−46] These xanthate-type CTAs were finally purified by column chromatography on silica with *n*-hexane/ethyl acetate (10/1 vol %) as the eluent.

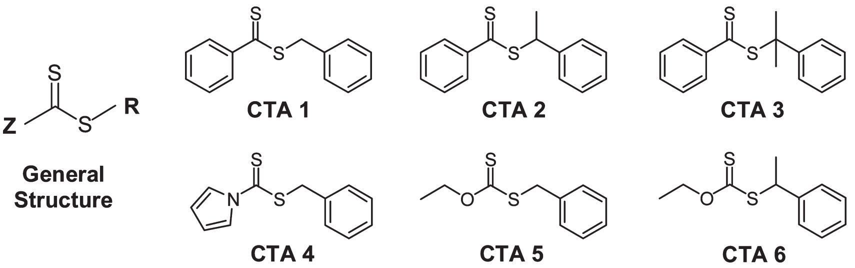
Synthesis of Vinylthiophene Derivatives. 2,5-Dibromo-3-vinylthiophene (DB3VT) was synthesized by Wittig reaction of 2,5-dibromo-3-thiophenecarboxaldehyde, which was prepared by bromination of 3-thiophenecarboxaldehyde. The bromination was carried out according to a procedure reported in the literature.[47] To a solution of 3-thiophenecarboxaldehyde (6.7 g, 0.06 mol) in 120 mL of chloroform was added anhydrous sodium bicarbonate (12.5 g, 0.15 mol), followed by the dropwise addition of a solution of bromine (25.0 g, 0.15 mol, in 150 mL of chloroform) over a period of 4 h. The reaction mixture was stirred overnight at room temperature and then filtered. The filtrate was washed with water (200 mL × 3) and dried over $MgSO_4$. After the filtration, the solvent was evaporated, and the solid residue was purified by column chromatography on silica with *n*-hexane/CH_2Cl_2 (2/1 vol %) as the eluent, followed by vacuum distillation to give the product as a light yellow solid (yield = 66%). The structure of 2,5-dibromo-3-thiophenecarboxaldehyde was confirmed by ^1H and ^{13}C NMR spectroscopy (see Figure S1a in the Supporting Information).

The monomer synthesis was conducted using 2,5-dibromo-3-thiophenecarboxaldehyde as follows: methyltriphenylphosphonium bromide (6.88 g, 0.0189 mol) and dry THF (70 mL) were placed in a three-necked flask. The hexane solution of *n*-BuLi (2.66 M, 6.8 mL, 0.0182 mol) was added dropwise to the mixture under a nitrogen atmosphere at 0 °C by external ice-bath cooling, and the resulting mixture was stirred at room temperature for 30 min. Then, 2,5-dibromo-3-thiophenecarboxaldehyde (4.00 g, 0.0145 mol) in dry THF (37.5 mL) was added gradually to the reaction mixture while it was kept at 0 °C. The stirring was continued at room temperature for about 4 h with TLC monitoring. The precipitate, which corresponds to phosphonium oxide, was filtered off, and the filtrate was dropped into diethyl ether (400 mL). After the mixture was stirred at room temperature for 2−3 h, the precipitate was filtered off and the filtrate was partially evaporated under reduced pressure. Then, the residue was dropped into hexane (500 mL), and it was stirred at room temperature for 2−3 h. Finally, the precipitate was filtered off, and the filtrate was evaporated under reduced pressure in the dark to give a crude product. The crude monomer was purified by column chromatography on silica with *n*-hexane as the eluent. The product was finally dried under vacuum at room temperature to yield DB3VT as a slightly yellow liquid (3.07 g, 79%). ^1H NMR ($CDCl_3$): δ 5.3, 5.6 (2d, 2H, $CH_2{=}CH-$), 6.5−6.7 (q, 1H, $CH_2{=}CH-$), 7.1 (s, 1H, heterocyclic). ^{13}C NMR ($CDCl_3$): δ 110.3, 111.8, 116.6 ($CH_2{=}CH-$), 127.5, 128.4 ($CH_2{=}CH-$), 139.4 ($CH_2{=}CH-C$). The ^1H and ^{13}C NMR spectra of the monomer are shown in Figures S1 and S2, respectively (see Supporting Information). Anal. Calcd for $C_6H_4Br_2S$: C, 26.89; H, 1.50; S, 11.97; Br, 59.64. Found: C, 26.86; H, 1.50; S, 12.14. Note that DB3VT was purified before the polymerization and treated carefully in the dark because it is susceptible to oxidation.

2-Vinylthiophene (2VT) and 3-vinylthiophene (3VT) were also synthesized by Wittig reaction of 2-thiophenecarboxaldehyde and 3-thiophenecarboxaldehyde, respectively, according to a method reported previously. Both monomers were distilled two times under vacuum (2VT: bp = 51 °C/3.0 kPa, lit.[13] 49−51 °C/3.0 kPa; 3VT: bp = 59 °C/4.0 kPa, lit.[17] 55−57 °C/4.0 kPa). The yield was 33% for 2VT and 27% for 3VT. The ^1H and ^{13}C NMR spectra of the monomers are shown in Figures S3 and S4, respectively (see Supporting Information).

General Polymerization Procedure. All polymerizations were carried out with AIBN as an initiator in a degassed sealed tube. A representative example is as follows: DB3VT (1.30 g, 4.9 mmol), CTA 2 (12.9 mg, 0.049 mmol), AIBN (0.80 mg, 0.0049 mmol), and dehydrated 1,4-dioxane (2.3 mL) 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 flame-sealed under vacuum, it was stirred at 60 °C for 24 h in the dark. The reaction was stopped by rapid cooling with liquid nitrogen. The reaction mixture was precipitated in a large excess of *n*-hexane and isolated by filtration. The resulting product was finally dried under vacuum at room temperature to yield poly(DB3VT) as a pale red powder. The polymer had M_n = 7300 and M_w/M_n = 1.07 according to GPC using polystyrene calibration and M_n = 21 100 determined using ^1H NMR in $CDCl_3$ by comparison of the area of the peak at 6.2−6.7 ppm (1H) corresponding to the heterocyclic ring in DB3VT repeating

Scheme 2. Structures of Chain Transfer Agents (CTAs) Used in This Study



units to the peak at 7.8−7.9 ppm (2H) corresponding to the dithiobenzoate end group. For the determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in $CDCl_3$ at room temperature, and the integration of the 4-position proton of the thiophene ring of the monomer (1H) at around 7.1 ppm was compared with the sum of the intensities of the thiophene ring of the polymer (1H) at 6.2−6.7 ppm and the monomer $CH_2{=}CH-$ resonance (1H) at 6.5−6.7 ppm. Conversion determined by this method was 73%. Monomer conversion (72%) could be also determined by the integration of one proton of the monomer resonance at 5.5−5.7 ppm compared with the methine proton of the polymer main chain at 2.1−2.7 ppm. In this study, the former method was mainly employed to determine the conversion of BD3VT because it can be applicable for both homopolymerization and copolymerization during the synthesis of block copolymers. Additionally, the polymer yield was gravimetrically determined from the *n*-hexane-insoluble polymer sample (yield = 69%, 0.91 g). The resulting polymer was soluble in THF, 1,4-dioxane, chloroform, *N*-methyl-2-pyrrolidone, and insoluble in *n*-hexane, diethyl ether, acetone, *N*,*N*-dimethylformamide, methanol, and water. ^{1}H NMR ($CDCl_3$): δ 1.1−1.9 (broad m, 2H, $CH_2{-}CH$), 2.1−2.7 (broad m, 1H, $CH_2{-}CH$), and 6.2−6.7 (broad m, 1H, heterocyclic H).

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

$$M_{\mathrm{n}}(\mathrm{theor}) = \frac{[\mathrm{monomer}]_0}{[\mathrm{CTA}]_0} \times M_{\mathrm{monomer}} \times \mathrm{conv} + M_{\mathrm{CTA}} \quad (1)$$

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

For the kinetic study, a mixed solution of DB3VT (2.32 g, 8.66 mmol), CTA 2 (22.4 mg, 0.0867 mmol), AIBN (1.42 mg, 8.66 μmol), and dry 1,4-dioxane (4.3 mL) was typically divided into five glass ampules, and each solution was then degassed by three freeze−evacuate−thaw cycles. The ampules were sealed by a flame under vacuum and then placed in a thermostatic oil bath at 60 °C in the dark for the desired time. The monomer conversion was determined by the ^{1}H NMR spectrum of the polymerization mixture as previously described.

Synthesis of Block Copolymers Using Poly(MMA) as a Macro-CTA. A representative example of the synthesis of the block copolymer composed of MMA and DB3VT is as follows: MMA (1.88 g, 18.8 mmol), cumyl dithiobenzoate (CTA 3, 51.4 mg, 0.189 mmol), AIBN (10.4 mg, 0.063 mmol), and dry 1,4-dioxane (4.7 mL) were placed in a dry ampule, 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 12 h. After the product was purified by precipitation into *n*-hexane, the resulting poly(MMA) ($M_{\mathrm{n,SEC}} = 6800$, $M_{\mathrm{n,NMR}} = 9000$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.19$, conversion = 68%) was employed as a macro-CTA. The molecular weight of poly(MMA) was calculated by comparison of the area of the peak at 3.3−3.8 ppm corresponding to three methoxy protons in MMA repeating units to the peak at 7.8−7.9 ppm corresponding to two protons of the dithiobenzoate end group.

The dithiobenzoate-terminated poly(MMA) (0.200 g, 0.022 mmol), AIBN (0.7 mg, 0.0044 mmol), DB3VT (0.290 g, 1.08 mmol), and 1,4-dioxane (1.1 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 in the dark (conversion determined by ^{1}H NMR spectroscopy = 58%). The reaction mixture was purified by reprecipitation into *n*-hexane and isolated by filtration to give a block copolymer, poly(MMA)-*b*-poly(DB3VT). The copolymer composition was determined using ^{1}H NMR spectroscopy by a comparison of peaks associated with the two comonomers. The peak at 6.2−6.7 ppm is attributed to the heterocyclic proton (1H) of DB3VT unit, whereas the peak at 3.3−3.8 ppm corresponds to the methoxy protons (3H) of the MMA unit.

Suzuki Coupling Reaction for Synthesis of Poly(vinylterthiophene). Under argon, poly(DB3VT) (10.6 mg, $M_{\mathrm{n}} = 6200$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.05$, 0.039 unit mmol), 2-thiopheneboronic acid (0.10 g, 0.789 mmol), $NaHCO_3$ (0.99 g, 11.8 mmol), and dry THF (5.0 mL) were placed in a 30 mL flask equipped with a condenser. The mixture was stirred at room temperature under an argon atmosphere until the homogeneous solution was obtained, and then 5.0 mL of distilled water was added to the mixture. Subsequently, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 9.1 mg, 7.9 mmol) dissolved in dry THF (1.0 mL) was dropped gradually into the mixture, and it was stirred in the dark under an argon atmosphere at 70 °C for 24 h. After this period, the reaction mixture was precipitated in a large excess of methanol and redissolved in THF, followed by reprecipitation into water. After the product was isolated by filtration, it was finally dried under vacuum at room temperature to yield the product as a brown powder: yield = 98% (11.3 mg), $M_{\mathrm{n,GPC}} = 8300$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.21$.

Suzuki Coupling Reaction for Synthesis of Cross-Linked Poly(MMA)-*b*-poly(DB3VT). In the case of the reaction of the block copolymer and difunctional boronic acid, poly(MMA)$_{91}$-*b*-poly(DB3VT)$_9$ ($M_{\mathrm{n}} = 12\,100$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.18$, 50 mg, 0.039 unit mmol), 2,5-thiophenediboronic acid (9.5 mg, 0.039 mmol), $NaHCO_3$ (0.066 g, 7.8 mmol), and dry THF (5.0 mL) were placed in a 30 mL flask under argon, and the mixture was stirred at room temperature. After the homogeneous solution was obtained, 5.0 mL of distilled water was added to the mixture. Then, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 4.5 mg, 3.9 mmol) dissolved in dry THF (1.0 mL) was dropped gradually into the mixture, and it was stirred in the dark under an argon atmosphere at 70 °C for 24 h. After this period, the reaction mixture was precipitated in a large excess of methanol and redissolved in THF, followed by reprecipitation into water and hexane. After the product was isolated by filtration, it was finally dried under vacuum at room temperature to yield the product as a brown powder: yield = 91% (43.7 mg), $M_{\mathrm{n,GPC}} = 74\,100$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 3.03$.

Instrumentation. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JEOL JNM-ECX400. The UV−vis spectra were recorded with a on a JASCO V-630BIO UV−vis spectrophotometer. Fluorescence spectra were obtained from a JASCO FP-6100 spectrofluorophotometer. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer.

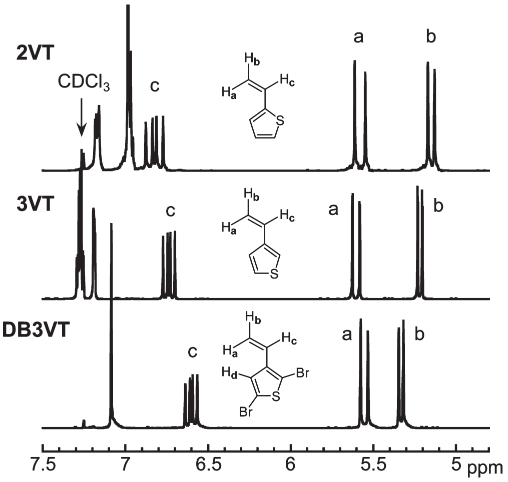


Figure 1. ^{1}H NMR spectra of three vinylthiophene derivatives ($CDCl_3$).

Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by GPC using a system consisting of a Tosoh DP-8020 pump and a Viscotek TDA model 301 triple detector array (RI, viscosity, and right-angle laser light scattering detector (RALLS); wavelength = 670 nm). The column set was as follows: a guard column [TSK guard column H_{XL}-H, 4.0 cm] and four consecutive columns [Tosoh TSK-GELs (exclusion limited molecular weight): GMH_{XL} (4×10^8), $G4000H_{XL}$ (4×10^5), $G3000H_{XL}$ (6×10^4), $G2500H_{XL}$ (2×10^4), 30 cm each] eluted with THF at a flow rate of 1.0 mL/min. Polystyrene standards were employed for calibration. GPC-RALLS was also performed to determine the absolute molecular weights of poly(DB3VT). The excess refractive index increment, dn/dc = 0.131 for poly(DB3VT), was measured in THF at 25 °C using a DRM1021 differential refractometer operating at 633 nm.

Results and Discussion

Screening of Reactions Conditions. Initially, we compared the conventional radical polymerization of three different vinylthiophene derivatives: 2-vinylthiophene (2VT), 3-vinylthiophene (3VT), and 2,5-dibromo-3-vinylthiophene (DB3VT). Bulk polymerization of vinylthiophene derivatives was conducted with AIBN at $[M]_0/[AIBN]_0 = 100$ (see Supporting Information, Table S1), in order to find conditions for obtaining polymeric product having relatively high molecular weight with sufficient yield. When the bulk polymerization of 2VT was conducted at 80−100 °C, polymers having low molecular weights (M_n = 2700−5200, M_w/M_n = 1.83−2.37) were obtained with relatively high monomer conversions (> 75%, as determined by ^{1}H NMR spectroscopy) after 48 h. RAFT polymerization of 2VT using several CTAs under different conditions also gave the polymers having low molecular weights and broad molecular weight distributions (M_n = 1900−4000, M_w/M_n = 1.67−2.79; see Supporting Information, Table S2). In the cases of the free radical polymerizations of 3VT in bulk, only 53% conversion was achieved at 100 °C even after 48 h. The molecular weights of poly(3VT)s were still low (M_n = 5800−7500, M_w/M_n = 2.00−2.23; Table S1), independent of the polymerization time (24−48 h) and the initiator concentration ([M]/[AIBN] = 100−200). Relatively low molecular weights of poly(2VT) and poly(3VT) could account for an inherent tendency of the propagating poly(2VT) and poly(3VT) radical to undergo chain transfer reactions.

When the free radical polymerization of the dibromo-substituted vinylthiophene derivative, DB3VT, was conducted in bulk at 80 °C for 24 h, in contrast, a polymer having relatively high molecular weight (M_n = 64 500, M_w/M_n = 3.06) was obtained with almost full conversion (97%). The polymerization at lower temperature (60 °C) led to the formation of the higher molecular weight product (M_n = 153 100, M_w/M_n = 2.73; see Supporting Information, Table S1). Under these conditions, the content of the ampule was completely solidified. Hence, we conducted the free radical polymerization of DB3VT in 1,4-dioxane ([M] = 2.0 mol/L), in which the polymerization proceeded homogeneously and the polymer having relatively high molecular weight with sufficient yield (M_n = 34 300, M_w/M_n = 2.40, conv = 94%) was obtained as a powder after precipitation into hexane. The comparison of chemical shifts of vinyl groups of the monomers evaluated by ^{1}H NMR spectroscopy (Figure 1) supported the different reactivity of DB3VT, compared with those of 2VT and 3VT. The ^{1}H NMR chemical shifts of vinyl groups of monomers were reported to be correlated with the reactivities of monomers.[48,49] These results suggest that incorporation of the bromide groups at the 2,5-positions on the thiophene ring in DB3VT leads to the improvement of the reactivity of the vinyl group, in addition to the suppression of unfavorable side reactions occurred on the thiophene ring. On the basis of these preliminary results, we selected DB3VT for our further investigations toward the precise synthesis of poly(vinylthiophene) derivatives having low polydispersity and controlled molecular weights.

Table 1. Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization of 2,5-Dibromo-3-vinylthiophene (DB3VT) in 1,4-Dioxane at 60 °C for 24 h[a]

run	CTA[b]	conv[c] (%)	M_n theory[d]	M_n SEC[e]	M_w/M_n[e]
1		94		34 300	2.40
2	CTA 1	89	24 000	15 700	1.36
3	CTA 2	95	25 800	9 300	1.13
4	CTA 3	91	24 700	8 000	1.16
5	CTA 4	99	26 800	23 300	1.79
6	CTA 5	99	26 800	29 400	2.19
7	CTA 6	97	26 200	56 700	1.91

[a] $[DB3VT]_0/[CTA]_0/[AIBN]$ = 200/2/1, $[DB3VT]_0$ = 2.0 mol/L. [b] See Scheme 2. [c] Calculated by ^{1}H NMR in $CDCl_3$. [d] The theoretical molecular weight ($M_{n,theory}$) = $[DB3VT]_0/[CTA]_0$ × (MW of monomer) × conv + (MW of CTA). [e] Determined by size exclusion chromatography using polystyrene standards in THF.

RAFT Polymerization of 2,5-Dibromo-3-vinylthiophene (DB3VT). In this study, three dithiobenzoate-type mediating agents having different R groups, benzyl dithiobenzoate (CTA 1), 1-phenylethyl dithiobenzoate (CTA 2), and cumyl dithiobenzoate (CTA 3), were selected as the CTA (Scheme 2). The effect of the R substitute on the effectiveness of CTA was initially investigated on the polymerization of DB3VT. We also employed dithiocarbamate-type (CTA 4) and xanthate-type (CTA 5, CTA 6) mediating agents for comparison. CTA 1, CTA 4, and CTA 5 have the same R group, which yields a benzyl radical species upon fragmentation.

The polymerization of DB3VT was conducted with different CTAs and AIBN as an initiator 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 CTA 3 in 1,4-dioxane, a polymer having a low polydispersity (M_w/M_n = 1.16) was obtained with a high conversion (91%, as determined by ^{1}H NMR spectroscopy). Almost full conversion (95%) was obtained for the polymerization with CTA 2, which also afforded poly(DB3VT) having a low polydispersity and

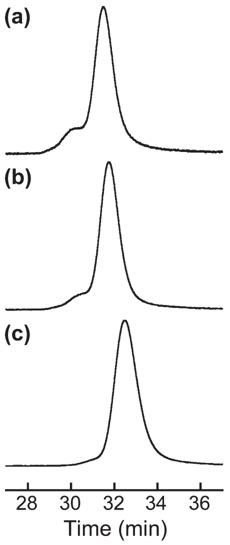


Figure 2. SEC traces of poly(DB3VT)s obtained by RAFT polymerization of DB3VT with CTA 2 in 1,4-dioxane at 60 °C for 24 h at different [CTA]/[AIBN] ratios: (a) [CTA]/[I] = 2, (b) [CTA]/[I] = 5, and (c) [CTA]/[I] = 10.

moderate molecular weight (M_n = 9300, M_w/M_n = 1.13). In both cases, a small shoulder peak at high molecular weight region can be detected in the SEC traces (see Figure 2a and Supporting Information), which is frequently observed for RAFT polymer obtained at high monomer conversion and is most probably attributed to species arising from bimolecular termination reactions of the growing polymer chains. The poly(DB3VT) obtained with CTA 1 showed broader polydispersity compared to those with CTA 2 and CTA 3. This may be due to the fact that the secondary and tertiary radicals, produced from CTA 2 and CTA 3, are more easily formed than the primary benzyl radical expelled from CTA 1, resulting in the faster consumption of CTA and uniform initiation. It was reported that static factors, radical stability, and polar factors all appeared to play an important role in determining the leaving group ability of R$^•$ (transfer coefficient) and the effectiveness of RAFT agents.[50] Although the leaving ability of the secondary R group in CTA 2 is lower than that with CTA 3, CTA 2 may show good balance between the leaving ability and reinitiation ability from the electron-donating phenylethyl moiety that is stabilized by aromatic conjugation. The polymerization with the dithiocarbamate-type CTA (CTA 4) afforded the poly(DB3VT) with a relatively broad polydispersity (M_w/M_n = 1.79). As expected, the polymerizations with the xanthate-type mediating agents (CTA 5 and CTA 6) provided the polymers with broader polydispersities. In general, xanthates are useful for controlling the radical polymerization of nonconjugated monomers (less activated monomers including *O*-vinyl and *N*-vinyl monomers).[51]

Table 2. Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization of 2,5-Dibromo-3-vinylthiophene (DB3VT) in 1,4-Dioxane at 60 °C for 24 h[a]

run	CTA[b]	$[\mathrm{CTA}]_0$/ $[\mathrm{AIBN}]_0$	conv[c] (%)	M_n theory[d]	M_n SEC[e] (NMR[c])	M_w/ M_n[e]
1	CTA 1	2	89	24 000	15 700	1.36
2		5	64	17 700	13 100	1.31
3		10	55	15 100	12 700	1.28
4	CTA 2	2	95	25 800	9 300 (33 900)	1.13
5		5	93	25 200	8 400 (29 700)	1.10
6		10	73	19 800	7 300 (21 100)	1.07
7	CTA 3	2	91	24 700	8 000 (36 100)	1.16
8		5	58	15 700	7 000 (25 500)	1.07

[a] $[\mathrm{DB3VT}]_0/[\mathrm{CTA}]_0$ = 100/1, $[\mathrm{DB3VT}]_0$ = 2.0 mol/L. [b] See Scheme 3. [c] Calculated by ^{1}H NMR in $CDCl_3$. [d] The theoretical molecular weight ($M_{n,\mathrm{theory}}$) = $[\mathrm{DB3VT}]_0/[\mathrm{CTA}]_0$ × (MW of monomer) × conv + (MW of CTA). [e] Determined by size exclusion chromatography using polystyrene standards in THF (RI detector).

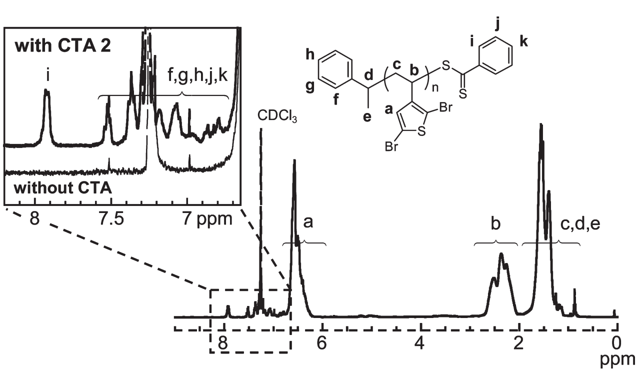


Figure 3. ^{1}H NMR spectrum ($CDCl_3$) of the dithiobenzoate-terminated poly(DB3VT) prepared by the polymerization with CTA 2.

The CTA/initiator ratio is one of key factors to determining the overall success of a RAFT polymerization with respect to control over the molecular weight and molecular weight distribution with a sufficiently fast polymerization rate.[52,53] In order to evaluate the effect of the CTA/initiator ratio, the polymerization of DB3VT was conducted with the dithiobenzoate-containing CTAs (CTA 1, CTA 2, CTA 3) at different $[\mathrm{CTA}]_0$:$[\mathrm{AIBN}]_0$ ratios between 2 and 10, keeping the monomer-to-chain transfer agent at a constant value of $[\mathrm{DB3VT}]_0/[\mathrm{CTA}]_0$ = 100/1. The polymerization was conducted in dry 1,4-dioxane at 60 °C for 24 h. The results are summarized in Table 2. In all cases, a higher $[\mathrm{CTA}]_0/[\mathrm{AIBN}]_0$ ratio led to lower polymer yield and narrower molecular weight distribution. As shown in Figure 2, a small shoulder peak at high molecular weight region is detected in the SEC chart of the poly(DB3VT) obtained at $[\mathrm{CTA}]_0$:$[\mathrm{AIBN}]_0$ = 2, and the intensity of the shoulder peak decreases with increasing the $[\mathrm{CTA}]_0$:$[\mathrm{AIBN}]_0$ ratio. A similar tendency was observed in the polymerization with CTA 3, in which the shoulder SEC peak observed at high molecular weight region decreases with increasing the $[\mathrm{CTA}]_0$:$[\mathrm{AIBN}]_0$ ratio (see Supporting Information). When the polymerization was carried out with CTA 3, the monomer conversion decreased from 91% to 58% as [CTA]/[AIBN] ratio increased from 2 to 5, indicating significant influence of the CTA/initiator ratio on the monomer conversion and suppression of the unfavorable bimolecular termination reactions. These results are consistent with the general tendency that higher CTA/initiator ratios (lower concentration of the initiator) may afford better overall control of the polymerization, due to a decrease in the number of radicals available for unfavorable side reactions, but result in longer polymerization time. Whereas, lower CTA/initiator ratios often result in faster polymerization rate but may lead to a less controlled polymerization system.

In all cases, the experimental molecular weights are lower than the theoretical ones. These discrepancies are believed to result from the difference in hydrodynamic volume between poly(DB3VT)s and the linear polystyrene standards used for GPC calibration. In order to clarify this point, NMR spectroscopy was used to determine the chain-end structure and

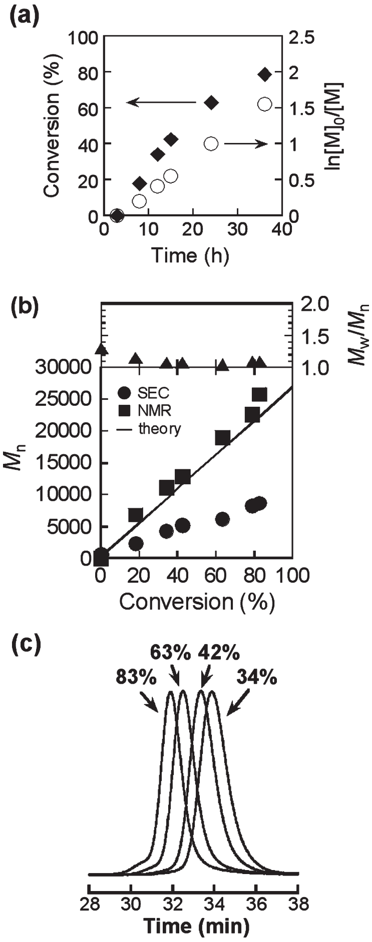


Figure 4. (a) Time−conversion (squares) and first-order kinetic (circles) plots for the polymerization of 2,5-dibromo-3-vinylthiophene (DB3VT) with 2,2′-azobis(isobutyronitrile) (AIBN) in the presence of (1-phenylethyl) dithiobenzoate (CTA 2, see Scheme 2) in 1,4-dioxane at 60 °C; [M] = 2.0 mol/L, [M]/[CTA]/[AIBN] = 1000/10/1. (b) Number-average molecular weight (circles: SEC; squares: NMR) and polydispersity (triangles) as a function of conversion. (c) Evolution of SEC traces of the products with conversion.

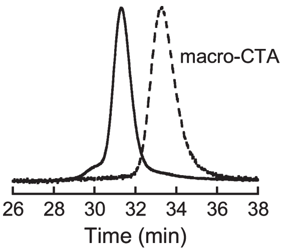


Figure 5. SEC traces of the parent poly(DB3VT) macro-CTA (dotted trace, $M_{\mathrm{n,NMR}}$ = 12 200, $M_{\mathrm{n,GPC}}$ = 5000, M_w/M_n = 1.08, conversion = 40%) obtained at [DB3VT]/[CTA 2]/[AIBN] = 1000/10/1 for 18 h at 60 °C and chain extended polymer (solid trace, $M_{\mathrm{n,NMR}}$ = 28 100, $M_{\mathrm{n,GPC}}$ = 9700, M_w/M_n = 1.15, conversion = 79%) obtained at [DB3VT]/[macro-CTA]/[AIBN] = 1000/10/1 for 24 h at 60 °C.

absolute molecular weights of poly(DB3VT)s. The ^{1}H NMR spectrum of the poly(DB3VT) obtained at [DB3VT]$_0$/[CTA 2]$_0$/[AIBN]$_0$ = 1000/10/1 is presented in Figure 3. The characteristic peaks at 1.1−1.9 ppm (C*H*$_2$CH in the backbone), 2.1−2.7 ppm (CH$_2$−C*H* in the backbone), and 6.2−6.7 ppm (heterocyclic proton) are clearly seen, which are attributed to poly(DB3VT) main chain. In addition to these peaks, aromatic resonances are clearly visible at 6.0−8.0 ppm, which correspond to the 1-phenylethyl and phenyl fragments at chain ends of the polymer. This is an indication that the polymer chain end is capped with the fragments of CTA as expected according to the mechanism of the RAFT process. The molecular weight of the polymer chain can be calculated by comparing the integrals of peaks for the chain-end protons to those of the main-chain protons. The molecular weight of poly(DB3VT) calculated by comparison of the area of the peak at 6.2−6.7 ppm corresponding to one proton of the heterocyclic ring (peak "a" in Figure 3) in DB3VT repeating units to the peak at 7.8−7.9 ppm (peak "i") corresponding to two protons of the dithiobenzoate end group is M_n = 21 100. The molecular weight determined by NMR is comparable to the theoretical value (M_n = 19 800) calculated using eq 1, which is apparently higher than that obtained from GPC using polystyrene standards ($M_{\mathrm{n,GPC}}$ = 7300). This spectroscopic method was also valid for the poly(DB3VT)s obtained with CTA 2 and CTA 3, independent of the [CTA]$_0$/[AIBN]$_0$ ratio, as shown in Table 2 and Figure S8 (Supporting Information).

The controlled/living character of the polymerization of DB3VT was studied by performing kinetics investigations in the presence of CTA 2 in dry 1,4-dioxane at 60 °C. Figure 4a shows the variations in the monomer conversion and ln ([M]$_0$/[M]$_t$) vs polymerization time for the polymerization with CTA 2. When the reaction was conducted at [DB3VT]$_0$/[CTA]$_0$/[AIBN]$_0$ = 1000/10/1, a relatively high conversion (79%) was reached after 36 h. A linear first-order kinetic plot is seen up to about 70% conversion (Figure 4a). As shown in Figure 4b, a linear increase in the number-average molecular weight with conversion suggests a constant number of propagating chains throughout the polymerization. The molecular weights determined by ^{1}H NMR are comparable to the theoretical values calculated using eq 1. The SEC traces (refractive index) of poly(DB3VT)s obtained at different reaction times are shown in Figure 4c. A progressive increase in the molar mass with conversion with narrow unimodal SEC peaks (M_w/M_n = 1.05−1.30) is evident and typical for a controlled/living polymerization.

GPC with a right-angle light scattering detector (GPC-RALLS) was utilized for the determination of the absolute molecular weights of representative samples of kinetic investigation. The polymers obtained at [DB3VT]$_0$/[CTA]$_0$/[AIBN]$_0$ = 1000/10/1 had $M_{\mathrm{n,GPC\text{-}RALLS}}$ = 10 400 (conversion = 34%), compared to $M_{\mathrm{n,calcd}}$ = 9400, $M_{\mathrm{n,NMR}}$ = 11 200, $M_{\mathrm{n,GPC}}$ = 4400 (M_w/M_n = 1.07); $M_{\mathrm{n,GPC\text{-}RALLS}}$ = 15 200 (conversion = 63%), compared to $M_{\mathrm{n,calcd}}$ = 17 200, $M_{\mathrm{n,NMR}}$ = 19 100, $M_{\mathrm{n,GPC}}$ = 6200 (M_w/M_n = 1.05); $M_{\mathrm{n,GPC\text{-}RALLS}}$ = 22 700 (conversion = 83%), compared to $M_{\mathrm{n,calcd}}$ = 22 400, $M_{\mathrm{n,NMR}}$ = 25 900, $M_{\mathrm{n,GPC}}$ = 8800 (M_w/M_n = 1.09), respectively (see Table S3 in Supporting Information). The molecular weights determined by GPC-RALLS are higher than the apparent ones obtained by conventional GPC. There were no significant differences between $M_{\mathrm{n,GPC\text{-}RALLS}}$ and $M_{\mathrm{n,calcd}}$, suggesting that the number of living polymer chains is comparable to that of the CTA. These results suggest good control of the polymerization of DB3VT, leading to the belief that the molecular weight of the thiophene-containing polymers can be easily adjusted by the [M]/[CTA] ratio.

An important criterion of the controlled/living character of the polymerization is the successful extension of a chain from a preformed polymer chain as a macro-CTA. To examine this point, the dithiobenzoate-terminated poly(DB3VT) ($M_{\mathrm{n,NMR}}$ = 12 200, $M_{\mathrm{n,GPC}}$ = 5000, M_w/M_n = 1.08) prepared by the polymerization using CTA 2, followed by purification via precipitation into *n*-hexane, was employed as a macro-CTA for chain extension experiments. After

Scheme 3. Synthesis of Block Copolymers by RAFT Polymerization of DB3VT Using (a) Poly(MMA) and (b) Poly(MA) as a Macro-Chain Transfer Agent

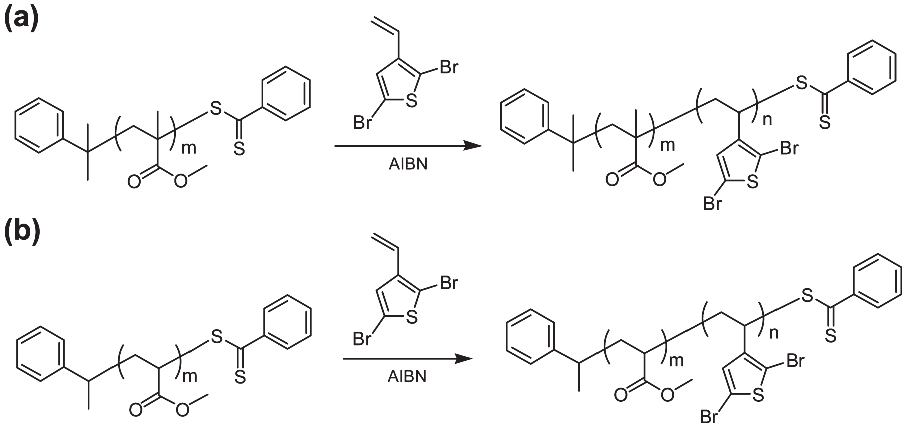


Table 3. Synthesis of Block Copolymers by Polymerization of 2,5-Dibromo-3-vinylthiophene (DB3VT) using 2,2′-Azobis-(isobutyronitrile) (AIBN) with Poly(methyl methacrylate) (Poly(MMA)) as a Macro-CTA in 1,4-Dioxane at 60 °C for 24 h[a]

run	$[\mathrm{DB3VT}]_0$/[macro-CTA]$_0$	conv[b] (%)	M_n theory[c]	M_n NMR[b]	M_n SEC[d]	M_w/M_n[d]	composition[b] (MMA:DB3VT)
1	50	58	16 800	17 600	8 500	1.19	73:27
2	100	62	25 400	26 600	10 800	1.14	57:43
3	400	11	20 900	32 400	12 400	1.14	50:50

[a] $[\text{macro-CTA}]_0/[\mathrm{AIBN}]_0 = 5$, $[\mathrm{DB3VT}]_0 = 1.0$ mol/L, macro-CTA = poly(MMA) ($M_{n,\mathrm{NMR}} = 9000$, $M_{n,\mathrm{GPC}} = 6800$, $M_w/M_n = 1.19$, conversion = 68%) prepared by CTA 3 (cumyl dithiobenzoate). [b] Determined by ^{1}H NMR in $\mathrm{CDCl_3}$. [c] The theoretical molecular weight ($M_{n,\mathrm{theory}}$) = $[\mathrm{DB3VT}]_0/[\mathrm{CTA}]_0 \times$ (MW of DB3VT) × conv + (MW of macro-CTA, $M_{n,\mathrm{NMR}} = 9000$). [d] Determined by size exclusion chromatography using polystyrene standards in THF (RI detector).

the chain extension, the resulting product was analyzed by SEC and compared to the original macro-CTA. When the chain extension was performed at 60 °C at the ratio $[\mathrm{DB3VT}]_0/[\text{macro-CTA}]_0/[\mathrm{AIBN}]_0 = 1000/10/1$, the monomer conversion was 79% after 24 h, and the polymer was isolated by precipitation in hexane. Figure 5 shows clear shifts in the SEC traces toward higher molecular weight regions after the chain extension, and the extended polymer exhibits a symmetrical SEC peak with a low polydispersity ($M_n = 9700$, $M_w/M_n = 1.15$). The molecular weight ($M_{n,\mathrm{NMR}} = 28\,100$) determined by ^{1}H NMR is comparable to the theoretical value ($M_{n,\mathrm{theory}} = 33\,600$) calculated by eq 1 using the molecular weight of the macro-CTA. These results suggest that most of the chain ends of the poly(DB3VT) are functionalized with the dithiobenzoate end groups, which can be used as a macro-CTA for a further chain extension reaction.

Synthesis of Block Copolymers. The synthesis of the block copolymer was conducted by RAFT polymerization of DB3VT using two macro-CTAs, poly(MMA) and poly(MA), as shown in Scheme 3. The dithiobenzoate-terminated poly(MMA) was prepared by RAFT polymerization in the presence of CTA 3, whereas poly(MA) having the dithiobenzoate end group was obtained with CTA 2. For the synthesis of well-defined block copolymers by RAFT process, the order of blocking is crucial. In this case, the first dithioester-terminated polymer (S═C(Z)S−A; A block corresponds to the first polymer, Z is the stabilizing group) should have a sufficient high transfer constant in the subsequent polymerization of second monomers to give B block.[54,55] 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 at approximately the same time.[56,57] On the basis of the consideration, we attempted the synthesis of the block copolymer by RAFT polymerization of DB3VT using the dithiobenzoate-terminated poly(MMA) and poly(MA).

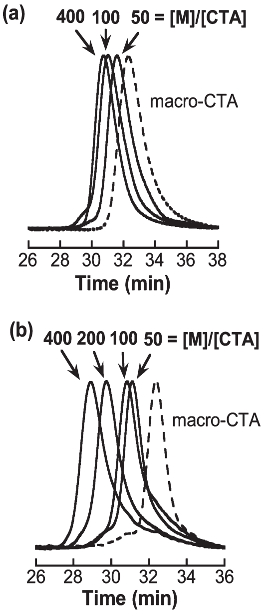


Figure 6. SEC traces of (a) the parent poly(MMA) macro-CTA (dotted trace, $M_{n,\mathrm{NMR}} = 9000$, $M_{n,\mathrm{GPC}} = 6800$, $M_w/M_n = 1.19$, conversion = 68%) and block copolymers, poly(MMA)-*b*-poly(DB3VT)s (solid traces), obtained by the polymerization at different [DB3VT]/[macro-CTA] ratios and (b) poly(MA) macro-CTA (dotted trace, $M_{n,\mathrm{NMR}} = 8400$, $M_{n,\mathrm{GPC}} = 7000$, $M_w/M_n = 1.11$, conversion = 58%) and block copolymers, poly(MA)-*b*-poly(DB3VT) (solid traces), obtained by the polymerization at different [DB3VT]/[macro-CTA] ratios.

The polymerization of DB3VT was conducted using the dithiobenzoate-terminated poly(MMA) in 1,4-dioxane at 60 °C for 24 h at different [M]/[macro-CTA] ratios between 50 and 400, maintaining the macro-CTA to initiator ratio at a constant value of $[\text{macro-CTA}]_0/[\mathrm{AIBN}]_0 = 5/1$. These results are summarized in Table 3. When the polymerization was conducted at $[\mathrm{DB3VT}]_0/[\text{macro-CTA}]_0 = 50-100$ ($[\mathrm{AIBN}]_0/[\text{macro-CTA}]_0/[\mathrm{M}]_0 = 1/5/250-500$), block copolymers having relatively narrow molecular weight distributJ. Am. Chem. Soc.ions ($M_w/M_n = 1.19$) were obtained with moderate yields. The molecular weight and the comonomer

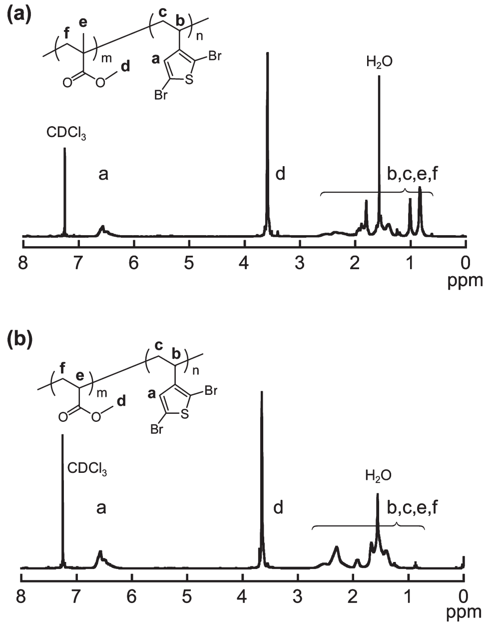


Figure 7. ^{1}H NMR spectra ($CDCl_3$) of (a) poly(MMA)-*b*-poly(DB3VT) and (b) poly(MA)-*b*-poly(DB3VT) obtained by the polymerization at [DB3VT]/[macro-CTA]=400 (see run 3 in Table 3 and run 4 in Table 4).

(DB3VT) composition of the resulting block copolymers increased with increasing the $[M]_0/[\text{macro-CTA}]_0$ ratios. As can be seen in Figure 6a, the SEC chromatograms of the starting macro-CTA and the growth polymers show that the molecular weight clearly shifts to lower elution time, which is consistent with increasing molecular weight. The composition of MMA and DB3VT determined by ^{1}H NMR (Figure 7) was comparable to the theoretical value calculated from the monomer conversion, M_n value of the macro-CTA and the monomer composition in the feed. The monomer conversion drastically decreased from 62% to 11%, as the $[M]_0/[\text{macro-CTA}]_0$ ratio increased from 100 to 400. Nevertheless, these results suggest a sufficient efficiency of the fragmentation from the intermediate radical to the dithiobenzoate-terminated poly(MMA) radical combined with an efficient reinitiation, resulting in the rapid conversion of the macro-CTA to the block copolymer under the conditions used in this study.

The synthesis of the block copolymer was also conducted by RAFT polymerization of DB3VT using dithiobenzoate-terminated poly(MA), which was prepared by RAFT polymerization of MA in the presence of CTA 2. The polymerization of DB3VT was carried out using the macro-CTA in 1,4-dioxane at 60 °C for 24 h. The reaction conditions, monomer conversion, molecular weights, polydispersities, and block copolymer compositions are summarized in Table 4. When the polymerization of DB3VT was conducted using the dithiobenzoate-terminated macro-CTA, the polymerization was relatively slow (conversion = 63% after 24 h at $[\text{DB3VT}]/[\text{macro-CTA}]/[\text{AIBN}]_0 = 250/5/1$). As shown in Figure 6b, low molecular weight species are detected in SEC curves, and some of the tails overlap substantially with the macro-CTA trace. The poly(MA) macro-CTA appears to have a high molecular weight shoulder (Figure 6b), which is commonly seen in MA RAFT polymerization, and the dead chains may have an effect on insufficient chain extension. Nevertheless, the molecular weight distributions remain relatively low (M_w/M_n = 1.23−1.31), and the molecular weights and the comonomer composition of the resulting block copolymers are comparable to the theoretical values. The block copolymers having different comonomer contents (DB3VT content determined by ^{1}H NMR = 25−63%) could be also obtained by the polymerization of DB3VT with the dithiobenzoate-terminated poly(MA).

Table 4. Synthesis of Block Copolymers by Polymerization of 2,5-Dibromo-3-vinylthiophene (DB3VT) Using 2,2′-Azobis-(isobutyronitrile) (AIBN) with Poly(methyl acrylate) (Poly(MA)) as a Macro-CTA in 1,4-Dioxane at 60 °C for 24 h[a]

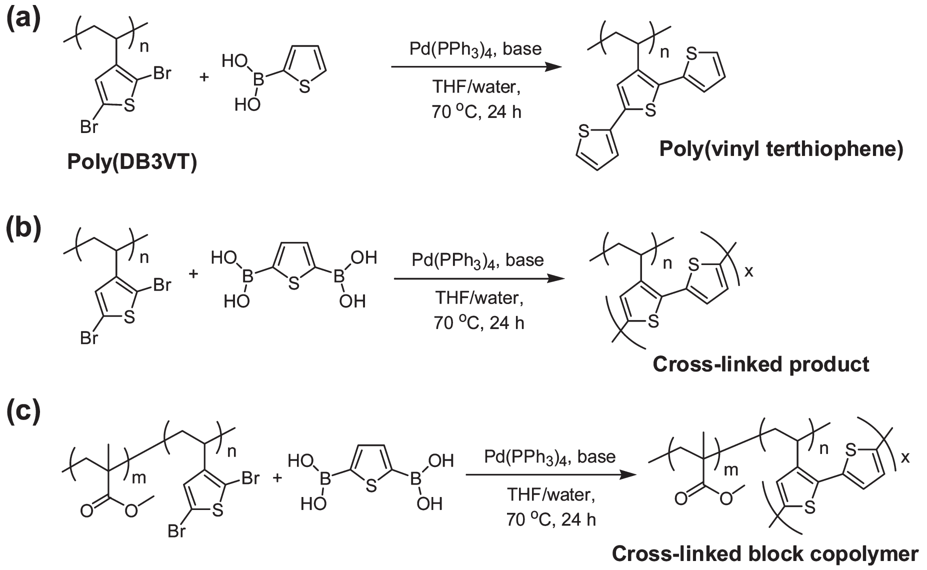
			M_n				
run	$[\text{DB3VT}]_0/[\text{macro-CTA}]_0$	conv[b] (%)	theory[c]	NMR[b]	SEC[d]	M_w/M_n[d]	composition[b] (MA: DB3VT)
1	50	63	16 900	16 900	8 500	1.29	75:25
2	100	40	19 500	19 800	8 600	1.31	69:31
3	200	53	36 900	30 900	14 700	1.23	53:47
4	400	36	47 000	51 600	18 500	1.31	37:63

[a] $[\text{macro-CTA}]_0/[\text{AIBN}]_0 = 5$, $[\text{DB3VT}]_0 = 1.0$ mol/L, macro-CTA = poly(MA) ($M_{n,NMR} = 8400$, $M_{n,GPC} = 7000$, $M_w/M_n = 1.11$, conversion = 58%) prepared by CTA 2 (1-phenylethyl dithiobenzoate). [b] Determined by ^{1}H NMR in $CDCl_3$. [c] The theoretical molecular weight ($M_{n,\text{theory}}$) = $[\text{DB3VT}]_0/[\text{CTA}]_0 \times$ (MW of DB3VT) × conv + (MW of macro-CTA, $M_{n,NMR} = 8400$). [d] Determined by size exclusion chromatography using polystyrene standards in THF (RI detector).

Suzuki Coupling Reaction. In order to confirm the versatility of the novel doubly polymerizable monomer, DB3VT, we investigated the modification of the 2,5-dibromide group of poly(DB3VT) and block copolymers by Suzuki coupling reaction using mono- and difunctional boronic acids. Initially, Suzuki coupling reaction of poly(DB3VT) using a monofunctional boronic acid was conducted with tetrakis-(triphenylphosphine)palladium(0) as a catalyst under basic conditions to afford poly(vinylterthiophene), as shown in Scheme 4a. The poly(DB3VT) ($M_{n,GPC}$ = 6200, M_w/M_n = 1.05) obtained by RAFT polymerization was reacted with a large excess of 2-thiopheneboronic acid in the presence of the Pd catalyst and $NaHCO_3$ in THF/water (1:1 vol %) at 70 °C for 24 h. Purification of the product was conducted by two precipitations into methanol and water, yielding a brown product, which was soluble in a number of organic solvents, such as chloroform and THF. The ^{1}H NMR spectrum of the product shows the characteristic broad peaks at 5.5−8.0 ppm (Figure 8), which are attributed to the terthiophenyl moiety. Conversion of the coupling reaction determined using ^{1}H NMR spectroscopy by a comparison of the aromatic peaks at 5.5−8.0 ppm (7H) to the peaks at 0.5−4.0 ppm attributed to the main chain (3H) was 77%, which is comparable to the value (71%) determined by elemental analysis (sulfur content). Figure 9 shows clear shifts in the SEC trace toward higher molecular weight region after the coupling reaction, and the polydispersity remains relatively low (M_n = 8300, M_w/M_n = 1.21), even if a small shoulder peak is detected at high molecular weight region. The molecular weight of the shoulder peak (M_p = 15 300) is roughly 2 times higher than that of the main product, suggesting a possibility that higher molecular weight peak is attributed to the coupling reaction. Note that Suzuki coupling reaction of poly(DB3VT) under different basic conditions (e.g., with KOH) led to the increase in the formation of the higher molecular weight product (see Figure S9 in Supporting Information). In contrast, Grignard displacement of the 2,5-dibromide group of poly(DB3VT) using (phenyl)magnesium bromide gave insoluble product.

Figure 10 depicts the absorption and fluorescence spectra of poly(DB3VT) and the product obtained by the coupling reaction in THF. The product exhibits absorption broad

Scheme 4. Suzuki Coupling Reaction of Poly(DB3VT) with (a) 2-Thiopheneboronic Acid, (b) 2,5-Thiophenediboronic Acid, and (c) Poly(MMA)-*b*-poly(DB3VT) with 2,5-Thiophenediboronic Acid



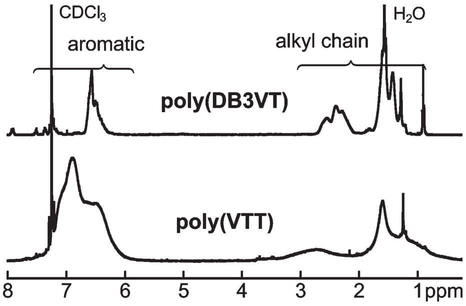


Figure 8. ^{1}H NMR spectra (CDCl$_3$) of poly(DB3VT) ($M_{n,GPC}$ = 6200, M_w/M_n = 1.05) and poly(vinylterthiophene), poly(VTT), obtained by Suzuki coupling reaction with 2-thiopheneboronic acid.

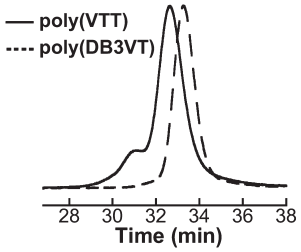


Figure 9. SEC curves of poly(DB3VT) (dotted line, $M_{n,GPC}$ = 6200, M_w/M_n = 1.05) and poly(vinylterthiophene), poly(VTT), obtained by Suzuki coupling reaction with 2-thiopheneboronic acid (solid line, $M_{n,GPC}$ = 8300, M_w/M_n = 1.21).

peak at around 336 nm, which is invisible in the spectrum of poly(DB3VT). In addition, a tiny absorption peak is detected at 250 nm, which is ascribed to the nonreacted dibromothiophene existed in the product. These results suggest that the most of 2,5-dibromide groups in the poly(DB3VT) are reacted with the monofunctional boronic acid to afford poly(vinylterthiophene), which may include a certain amount of dithiophene derivative. In the fluorescence spectra, only the product obtained by the coupling reaction shows the emission in the range of 400 and 600 nm, whereas no peak is detected in the poly(DB3VT).

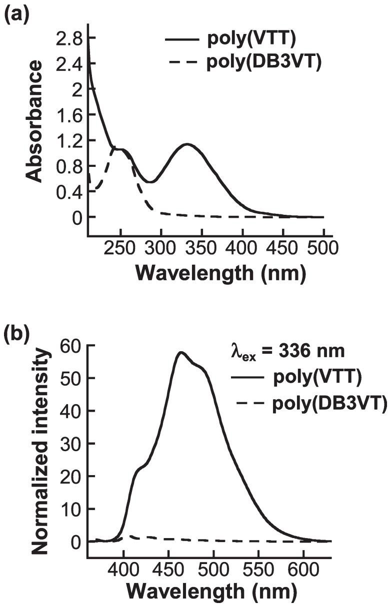


Figure 10. (a) Absorption and (b) fluorescence spectra of poly(DB3VT) and poly(vinylterthiophene), poly(VTT) (concentration = 2.4 × 10^{-5} terthiophene unit mol/L in THF).

In the next stage, a difunctional boronic acid, 2,5-thiophenediboronic acid, was employed as a coupling agent. The cross-linking reaction was conducted by treating the homopolymer, poly(DB3VT), with the difunctional boronic acid under similar conditions (Scheme 4b). The solid was isolated by reprecipitation into methanol, followed by Soxhlet extraction with THF. The color of the insoluble product after drying was brown, which was different from pale red color of poly(DB3VT) (see Supporting Information). The cross-linking reaction using the difunctional boronic acid was extended to the block copolymer, poly(MMA)-*b*-poly(DB3VT), as shown in Scheme 4c. When the cross-linking reaction was conducted with a block copolymer having low poly(DB3VT) content, poly(MMA)$_{91}$-*b*-poly(DB3VT)$_9$, a soluble product having a high molecular weight (M_n = 74 100, M_w/M_n = 3.03) was obtained after precipitations into methanol and water, as can be seen in Figure 11. Absorption and fluorescence spectra (THF) of the soluble composite, which can be regarded as a cross-linked block copolymer, are shown in Figure 12. The soluble composite absorbs light in the range

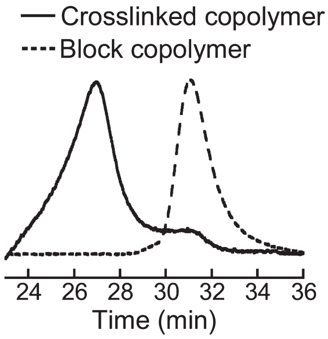


Figure 11. SEC curves of poly(MMA)$_{91}$-*b*-poly(DB3VT)$_9$ and cross-linked block copolymer prepared by Suzuki coupling reaction using 2,5-thiophenediboronic acid.

from 300 to 540 nm. The emission maximum of the soluble composite excited at 380 nm is observed at 521 nm, which may stem from the extended π-structure. Actually, the soluble composite (cross-linked block copolymer) exhibited a yellow fluorescence upon excitation at 365 nm (see photographs in Supporting Information). From these results, it is reasonable to consider that a selective dehalogenation of poly(DB3VT) segment in the block copolymer occurs effectively through the brominated thienyl group to give solid composite having a specific structure, such as core–shell particles having poly(thiophene) core and poly(MMA) shell.

The structure of the soluble composite (cross-linked block copolymer) obtained by Suzuki coupling reaction of poly(MMA)$_{91}$-*b*-poly(DB3VT)$_9$ using 2,5-thiophenediboronic acid is proposed to be similar to that of so-called core-cross-linking micelles.[58−64] In general, the core-cross-linking micelles can be prepared by conventional two-step reactions: micellization of the block copolymer in a selective solvent and subsequent cross-linking reaction of the interior part. In, contrast, the system developed in this study can be regarded as a one-step cross-linking of one of the blocks in a nonselective solvent. A similar one-step approach to core-stabilized nanoparticles was reported previously,[65] in which the particle formation of a block copolymer, polystyrene-*b*-poly(4-vinylpyridine), took place at high concentration upon the addition of a coupling agent without a micellization step. They demonstrated that the presence of non-cross-linkable polystyrene block prevented gelation, and an increase in the polystyrene length resulted in a considerable improvement in the structural regularity. Similarly, in our system, long poly(MMA) segment in the block copolymer may play a crucial role in preventing gelation and may confine the cross-linking reaction to isolated regions. Another assumption is the formation of core-cross-linking micelles by conventional two-step reactions: micellization of the block copolymer in a selective solvent and subsequent cross-linking reaction of the poly(DB3VT) segment. Poly(DB3VT) was insoluble in THF/water (1:1 vol %), which was employed as a solvent for Suzuki coupling reaction, whereas the poly(MMA) was swollen in the mixed solvent. Hence, the system can be composed of a poly(MMA) shell and a poly(DB3VT) core that can be cross-linked by the reaction with the difunctional boronic acid. Further studies on the relationship between the optoelectronic properties and the core-cross-linking micelle formation of the block copolymers having different compositions and chain lengths are now in progress.

Conclusion

In this study, we developed the novel doubly polymerizable monomer, DB3VT, that can undergo controlled radical polymerization via RAFT process, followed by Suzuki coupling reaction. Well-defined homopolymers and block copolymers consisting of poly(DB3VT) could be obtained by RAFT polymerization under suitable conditions. Modifications of the 2,5-dibromide group of poly(DB3VT) by Suzuki coupling reaction using the monofunctional boronic acid proceeded effectively to produce poly(vinylterthiophene) containing a certain amount of dithiophene derivatives. In contrast, difunctional boronic acid was used as a cross-linking agent to afford the network material from the homopolymer and soluble composite having an extended π-structure from the block copolymer with cross-linkable poly(DV3VT). The novel doubly polymerizable monomer, DB3VT, can be acted as a bridge between the controlled/living radical polymerization and poly(thiophene) chemistries. We believe that this paper represents the first report on controlled radical polymerization of the vinylthiophene having doubly polymerizable property, DB3VT, via RAFT and the synthesis of the block copolymers containing cross-linkable poly(DB3VT) segments, which can be regarded as a precursor for the production of highly ordered polythiophene derivatives via self-assembly.

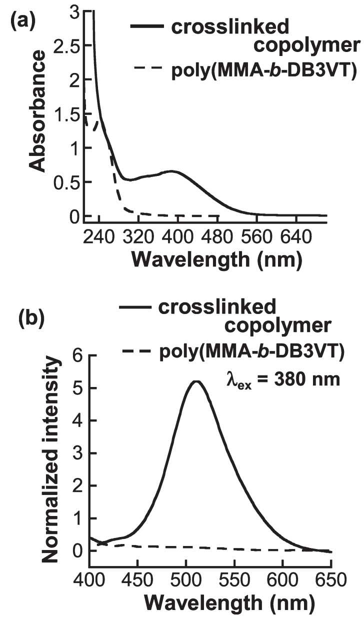


Figure 12. (a) Absorption and (b) fluorescence spectra (concentration = 1×10^{-4} dithiophene unit mol/L in THF).

Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of three vinylthiophene derivatives, GPC traces of poly(DB3VT)s prepared under different conditions and poly(vinylterthiophene)s obtained using different bases, ^{1}H NMR spectra of poly(DB3VT)s prepared with different CTAs, tables summarizing the data of free radical polymerization of three vinylthiophene derivatives, RAFT polymerization of 2VT, kinetic results of RAFT polymerization of DB3VT, and appearance of samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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