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RAFT Polymerization of Vinyl Sulfonate Esters for the Controlled Synthesis of Poly(lithium vinyl sulfonate) and Sulfonated Block Copolymers

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ABSTRACT: Four vinyl sulfonate ester derivatives, neopentyl ethenesulfonate (NES), 1-butyl ethenesulfonate (BES), isopropyl ethenesulfonate (IPES), and phenyl ethenesulfonate (PES), were polymerized by conventional radical polymerization and reversible addition–fragmentation chain transfer (RAFT) polymerization. Three xanthate-type chain transfer agents (CTAs), a dithiocarbamate-type CTA, and a dithioester-type CTA were compared for these RAFT polymerizations. Among various CTAs, *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate was the most efficient to obtain poly(NES) and poly(BES) having low polydispersities. The effects of several parameters, such as temperature and CTA to initiator molar ratio, were examined in order to determine the conditions, leading to optimal control of the polymerization. With the xanthate-type CTA under suitable conditions, reasonable control of the polymerization of NES was confirmed by the formation of the relatively low polydispersity products, linear increase in the molecular weight with the conversion, and feasibility in the control of the molecular weight based on the ratio of monomer consumed to the amount of CTA used. The polymerization behavior of BES was comparable to that of NES. Deprotection of the neopentyl group of the poly(NES) proceeded smoothly to give water-soluble poly(lithium vinyl sulfonate). Synthesis of the well-defined block copolymer involving the poly(lithium vinyl sulfonate) segment was conducted by RAFT polymerization of NES using poly(*N*-vinylcarbazole) macro-CTA, followed by deprotection.

Introduction

Poly(vinyl sulfonic acid) and its salt forms are one of the simplest and most important sulfonic acid-containing polymers that have been applied in a large variety of areas. An advantage of these polymers is the highest content of the sulfonate group in the polymer, in which the sulfonate moiety is directly linked to the polymer main chain. Since poly(vinyl sulfonic acid) possesses negatively charged sulfonate groups, it represents a class of water-soluble polymers and anionic polyelectrolytes. Specific interactions, such as acid–base interactions and oppositely charged ionic interactions, between poly(vinyl sulfonic acid)-based materials and biologically active molecules have attracted much academic and technological interest.[1−6] For example, various copolymers[1,7,8] and hydrogels[2] composed of poly(vinyl sulfonic acid) have been developed as blood compatible materials, smart materials, and a platform for cationic drug delivery systems, which are mainly due to the fact that negatively charged sulfonate groups reduce protein adsorption or platelet adhesion. Poly(vinyl sulfonic acid)–protein interactions have been also investigated[3,4] because the nature of the polyelectrolyte acts as a crucial factor to determine the efficiency of protein precipitation (protein isolation) and the formation of stable protein–polyelectrolyte complexes.

In addition to biorelated applications, much attention has been devoted to the interaction between poly(vinyl sulfonic acid) and dyes since the aggregation of the dyes can be modified by a charged polyelectrolyte.[9−11] Poly(vinyl sulfonic acid) and its copolymers have been also used as an accelerator for reduction reactions[12,13] and as a polychelatogen to bind metal ions.[14] In an all-solid supercapacitor based on polyaniline and sulfonated polymers, poly(vinyl sulfonic acid) was employed as a proton conducting solid electrolyte.[15] Other examples involve surface-grafted poly(vinyl sulfonic acid) as a new class of heterogeneous acid catalyst[16] and polymer-enhanced ultrafiltration using poly(vinyl sulfonic acid) for metal ion recovery.[17] In most of these works, salt forms of poly(vinyl sulfonic acid), such as poly(sodium vinyl sulfonate) and poly(potassium vinyl sulfonate), were employed because of the difficulties in the purification of the acid form of the monomer, vinyl sulfonic acid, and in the cationic exchange of the sodium form of the polymer, poly(sodium vinyl sulfonate). Recently, free radical polymerization of high-purity vinyl sulfonic acid in water was reported to yield poly(vinyl sulfonic acid) exhibiting very high acidic proportions (ion-exchange capacity; IEC = 9.2 meq g^{-1}).[16]

Sulfonic acid-containing block copolymers are an area of increasing interest, which is mainly due to their feasibility in the creation of a highly ordered structure as a result of self-organization and potential applications for proton conductive membranes.[18−22] Attempts to synthesize well-defined polymers containing the sulfonic acid groups using controlled radical polymerizations have appeared in the literature. Nitroxide-mediated polymerization and atom transfer radical polymerization of sodium styrenesulfonate have been frequently employed for the synthesis of various sulfonated block copolymers.[23−26] Direct reversible addition–fragmentation chain transfer (RAFT) polymerization of various ionic monomers having sulfonate moieties in the side chains have

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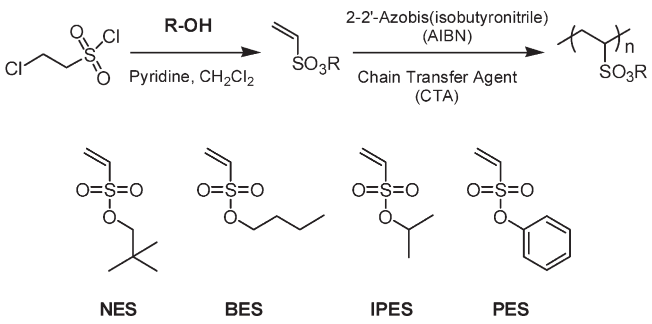
Scheme 1. Synthesis of Vinyl Sulfonate Esters and Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization



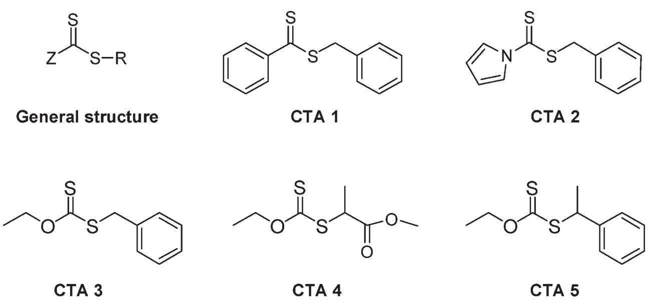
been reported, including styrene, acrylamide, and (meth)acrylates derivatives.[27,28] Sulfonic acid-containing block copolymers were also synthesized by controlled radical polymerization of styrene derivatives with protected sulfonic acid groups, followed by deprotection.[29,30] Although much attention has been directed toward the design and synthesis of novel sulfonic acid-containing block copolymers, to the best of our knowledge, the synthesis of well-defined poly(vinyl sulfonic acid) in both acid and salt forms by controlled radical polymerization has never been described before.

We now report the synthesis of the salt form of poly(vinyl sulfonic acid) with predetermined molecular weights and low polydispersity by RAFT polymerization of vinyl sulfonate esters, followed by deprotection. Several reports have been published on the conventional radical polymerization of vinyl sulfonate esters. Overberger et al. reported radical copolymerization of butyl vinylsulfonate with various comonomers including styrene, methyl acrylate, vinyl acetate, vinylidene chloride, and vinyl chloride.[31] They demonstrated that butyl vinyl sulfonate is compatible in reactivity to vinyl acetate and vinyl chloride, and that Q and e values of butyl vinylsulfonate are $Q = 0.021$, $e = 0.84$. Ueda et al. reported the radical polymerization of vinyl sulfonates having various substituent groups for the syntheses of poly(vinyl sulfonate)s and their random copolymers, which were employed as photoresist materials for 157 nm lithography.[32−34] In this study, we selected four vinyl sulfonate esters having different substituent groups, in order to understand the polymerization mechanism of this class of monomers. In the first part, we briefly compare the free radical polymerization behavior of four vinyl sulfonate esters, neopentyl ethenesulfonate (NES), 1-butyl ethenesulfonate (BES), isopropyl ethenesulfonate (IPES), and phenyl ethenesulfonate (PES), as shown in Scheme 1. Then, we describe RAFT polymerization of selected monomers, NES and BES, using suitable chain transfer agents (CTAs) under various conditions, and the deprotection of the neopentyl group of poly(NES). Finally, the synthesis of the well-defined block copolymer involving the poly(lithium vinyl sulfonate) segment was conducted by RAFT polymerization of NES using macro-CTA, followed by deprotection.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Chemical, >95%), 2-chloroethanesulfonyl chloride (Tokyo Kasei Kogyo, >95%), 2,2-dimethyl-1-propanol (Aldrich, >99%), 1-butanol, (Kanto Chemical, >99.0%), 2-propanol (Kanto Chemical, 99.5%), and pyridine (Kanto Chemical, >99.5%) were used as received. Phenyl ethenesulfonate (PES, Aldrich, 95%) used as a monomer was purified by column chromatography on silica with *n*-hexane/diethyl ether (60/40 vol-%) as the eluent. *N*-Vinylcarbazole (NVC, Tokyo Kasei, 98%) was recrystallized two times from methanol. Other materials were used without further purification.

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



Synthesis of Chain Transfer Agents (CTA)s. Five different CTAs were employed in this study, as shown in Scheme 2. Benzyl dithiobenzoate (CTA 1)[35,36] and benzyl 1-pyrrolecarbodithioate (CTA 2)[37,38] were synthesized according to the procedures reported previously. *S*-Benzyl-*O*-ethyl dithiocarbonate (CTA 3),[39−41] *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate (CTA 4),[42,43] and *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 5)[39,41,44] 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-bromoethyl benzene 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 Vinyl Sulfonate Esters. Three vinyl sulfonate esters having different substituent groups, neopentyl ethenesulfonate (NES), 1-butyl ethenesulfonate (BES), and isopropyl ethenesulfonate (IPES), were synthesized by the reaction of 2-chloroethanesulfonyl chloride with corresponding alcohols according to a previously reported method with slight modifications (Scheme 1).[33,45,46] In a typical experiment for the synthesis of neopentyl ethenesulfonate (NES), 12.5 mL of 2-chloroethanesulfonyl chloride (19.4 g, 0.12 mol) was added dropwise to a solution of 2,2-dimethyl-1-propanol (5.29 g, 0.060 mol) in 150 mL of dichloromethane under stirring at room temperature. Then, 19.4 mL of pyridine (19.0 g, 0.24 mol) was added dropwise to the reaction mixture, which was cooled during the addition. The reaction mixture was stirred at room temperature for 2 h and then filtered. The filtrate was washed with 10% Na$_2$CO$_3$ aqueous solution (100 mL × 3) and water (100 mL), and dried over MgSO$_4$. After the organic solvent was evaporated, the residue was purified by column chromatography on silica with *n*-hexane/diethyl ether (60/40 vol-%) as the eluent to give the product as a transparent liquid (5.95 g, 56%). ^{1}H NMR (CDCl$_3$): δ 6.5 (dd, 1H, CH$_2$=C*H*-), 6.4 (d, 1H, C*H*$_2$=CH−), 6.1 (d, 1H, C*H*$_2$=CH−), 3.7 (s, 2H, C*H*$_2$-C(CH$_3$)$_3$), 0.9 (s, 9H, CH$_2$−C(C*H*$_3$)$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 132.4 (CH$_2$=*C*H-), 130.2 (*C*H$_2$=CH−), 79.9 (*C*H$_2$−C(CH$_3$)$_3$), 31.7 (CH$_2$-*C*(CH$_3$)$_3$), 26.0 (CH$_2$−C(*C*H$_3$)$_3$) ppm. Anal. Calcd for C$_7$H$_{14}$O$_3$S: C, 47.17; H, 7.92; S, 17.99. Found: C, 47.04; H, 7.86; S, 17.83.

The same procedure was employed for the synthesis of 1-butyl ethenesulfonate (BES). The reaction of 2-chloroethanesulfonyl chloride with 1-butanol was conducted in the presence of pyridine at room temperature for 2 h. The purification of the crude product was carried out by washing with 10% Na$_2$CO$_3$ aqueous solution and water, followed by column chromatography on silica with *n*-hexane/diethyl ether (60/40 vol-%) to afford BES as a transparent liquid (44%). ^{1}H NMR (CDCl$_3$): δ 6.5 (dd, 1H, CH$_2$=C*H*-), 6.4 (d, 1H, C*H*$_2$=CH−), 6.1 (d, 1H, C*H*$_2$=CH−), 4.1 (t, 2H, −C*H*$_2$−CH$_2$−CH$_2$−CH$_3$), 1.7 (m, 2H, −CH$_2$−C*H*$_2$-CH$_2$−CH$_3$), 1.4 (m, 2H, −CH$_2$−CH$_2$−C*H*$_2$-CH$_3$), 0.9 (t, 3H, −CH$_2$−CH$_2$−CH$_2$−C*H*$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 132.6 (CH$_2$=*C*H-), 130.1 (*C*H$_2$=CH−), 70.8 (−*C*H$_2$−CH$_2$−CH$_2$−CH$_3$), 31.0 (−CH$_2$-*C*H$_2$−CH$_2$−CH$_3$), 18.7 ($-CH_2-CH_2\text{-}\mathit{C}H_2-CH_3$), 13.5 ($-CH_2-CH_2-CH_2\text{-}\mathit{C}H_3$) ppm. Anal. Calcd for $C_6H_{12}O_3S$: C, 43.88; H, 7.37; S, 19.53. Found: C, 44.11; H, 7.40; S, 19.74.

Similarly, isopropyl ethenesulfonate (IPES) was synthesized by the reaction of 2-chloroethanesulfonyl chloride with isopropanol. In this case, the column purification was conducted on silica with *n*-hexane/ethyl acetate (40/60 vol-%) as the eluent. IPES was obtained as a transparent liquid (45%). ^{1}H NMR ($CDCl_3$): δ 6.5 (dd, 1H, $CH_2{=}\mathit{CH}$-), 6.4 (d, 1H, $\mathit{CH_2}{=}CH-$), 6.0 (d, 1H, $\mathit{CH_2}{=}CH-$), 4.8 (m, 1H, $-\mathit{CH}\text{-}(CH_3)_2$), 1.4 (d, 6H, $-CH\text{-}(\mathit{CH_3})_2$) ppm. ^{13}C NMR ($CDCl_3$): δ 133.7 ($CH_2{=}\mathit{C}H$-), 129.1 ($\mathit{C}H_2{=}CH-$), 77.8 ($-\mathit{C}H\text{-}(CH_3)_2$), 23.0 ($-CH\text{-}(\mathit{C}H_3)_2$) ppm. Anal. Calcd for $C_5H_{10}O_3S$: C, 39.98; H, 6.71; S, 21.35. Found: C, 39.94; H, 6.71; S, 21.70.

^{1}H and ^{13}C NMR spectra and the solubility of these monomers are shown in Figures S1−3 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: NES (0.40 g, 2.2 mmol), CTA 4 (9.2 mg, 0.044 mmol), and AIBN (3.6 mg, 0.022 mmol) were placed in a dry glass ampule equipped with a magnetic stirr bar, and then the solution was degassed by three freeze−evacuate−thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 45 °C for 48 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 ^{1}H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in $CDCl_3$ at room temperature. The integration of the methyl protons of the neopentyl group in both monomer and polymer (9H) at 0.8−1.2 ppm was compared with the monomer $\mathit{CH_2}{=}CH$- resonance (1H) at around 6.1 ppm. Conversion determined by this method was 78%. The crude sample was directly employed without any purification for the GPC measurement. The crude polymer had M_n = 3900 and M_w/M_n = 1.34 according to GPC (THF) using polystyrene calibration.

The resulting poly(NES) was soluble in *n*-hexane, diethyl ether, acetone, THF, 1,4-dioxane, chloroform, methanol, DMF, and DMSO, and insoluble only in water. The solubility of poly(NES) is almost the same as that of the monomer, NES. For the ^{1}H NMR measurement and chain extension experiment, the crude poly(NES) was purified by dialysis using a Spectra/Por dialysis tube (MWCO: 1000) against methanol for 2 days. ^{1}H NMR ($CDCl_3$): δ4.2−3.8 (s, 2H, $\mathit{CH_2}\text{-}C(CH_3)_3$), 4.2−3.2 (br, 1H, *CH* in the polymer main chain), 2.8−1.6 (br m, 2H, $\mathit{CH_2}$ in the polymer main chain), 1.2−0.8 (s, 9H, $CH_2-C(\mathit{CH_3})_3$) ppm.

In the case of the polymerization of BES and IPES, the crude polymers were poured into a large excess of hexane and isolated by decantation. In contrast, the purification of the crude polymer obtained by the polymerization of PES was conducted by reprecipitation into a large excess of diethyl ether. All polymers were soluble in acetone, THF, chloroform, and insoluble in water, regardless of the structure. The solubilities of these polymers in various solvents are summarized in Table S1 (see Supporting Information).

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

$$M_n(\text{theor}) = \frac{[\text{Monomer}]_0}{[\text{CTA}]_0} \times M_{\text{Monomer}} \times \text{conv.} + M_{\text{CTA}} \quad (1)$$

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

Deprotection of Poly(NES). Deprotection of poly(NES) was conducted according to a previously reported procedure with slight modifications.[47] Poly(NES) (0.30 g, 1.7 unit mmol), LiBr (0.73 g, 8.4 mmol), and 2-butanone (10 mL) were placed in a flask, and the mixture was refluxed for 24 h. During the reaction, the mixed solution was changed gradually into a heterogeneous system. After the reaction, the precipitate, which corresponds to the lithium salt of the deprotected polymer, was filtered. The crude solid was dissolved in a small amount of methanol, and then it was purified by precipitation into diethyl ether. Finally, the resulting product was isolated by filtration, and then dried under vacuum at room temperature to give poly(lithium vinyl sulfonate) as a white solid (0.17 g, 86%). ^{1}H NMR (D_2O): δ 4.2−2.6 (1H, C*H* in the main chain), 2.6−1.3 (2H, C$\mathit{H_2}$ in the main chain).

Synthesis of Block Copolymers. A representative example of the synthesis of the block copolymer composed of NES and NVC is as follows: NVC (2.00 g, 10.3 mmol), CTA 4 (86.2 mg, 0.414 mmol), AIBN (34.0 mg, 0.207 mmol), and 1,4-dioxane (3.0 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 3 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(NVC) as a white solid (2.01 g, 95%, M_n = 3400 g/mol, M_w/M_n = 1.16), which was employed as a macro-CTA.

The dithiocarbonate-terminated poly(NVC) (66.5 mg, 0.020 mmol), AIBN (1.6 mg, 0.010 mmol), NES (0.35 g, 2.00 mmol), and chlorobenzene (0.18 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 methanol and isolated by filtration to give a block copolymer, poly(NVC)-*b*-poly(NES), as a white solid. Note that there was no poly(NES) impurity in the resulting block copolymer. If the homopolymer is formed by the homopolymerization of NES, it should be removed by the precipitation into methanol. The block copolymer was soluble in THF, chloroform, DMF, and insoluble in diethyl ether, hexane, methanol, and water.

The copolymer composition was determined using ^{1}H NMR spectroscopy by a comparison of peaks associated with the two comonomers. The 0.8−1.2 ppm is attributed to the methyl protons of the neopentyl moiety in the NES unit, whereas the peaks at 4.2−8.4 ppm correspond to the aromatic protons (8H) of the NVC unit. Thus, the comonomer composition can be calculated using eq 2 as follows:

$$\frac{8(x)}{9(1-x)} = \frac{\text{integral at } 4.2-8.4 \text{ ppm}}{\text{integral at } 0.8-1.2 \text{ ppm}} \quad (2)$$

Here x is the fraction of the NVC and $1 - x$ is the fraction of NES in the block copolymer.

Instrumentation. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JEOL JNM-ECX400. FT-IR spectra were obtained with a JASCO FT/IR-210 spectrometer. Thermogravimetric analysis (TGA) was performed on a SEIKO TGA/6200 at a heating rate of 10 °C/min under N_2. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer.

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 columns [Tosoh TSK-GELs (bead size, exclusion limited molecular weight), G4000H$_{XL}$ (5 μm, 4 × 10^5); G3000H$_{XL}$ (5 μm, 6 × 10^4); G2000H$_{XL}$ (5 μm, 1 × 10^4); 30 cm each] and a guard column [TSK-guardcolumn H$_{XL}$-L, 4 cm]. The system was operated at a flow rate of 1.0 mL/min, using THF as an eluent. Polystyrene standards were employed for calibration.

Table 1. Free Radical Polymerization of Vinylsulfonate Esters[a]

entry	monomer[b]	initiator[c]	temp (°C)	time (h)	conv.[d] %	M_n[e] (SEC)	M_w/M_n[e] (SEC)
1	NES	AIBN	60	24	91	5000	2.04
2		AIBN	45	48	84	8300	1.98
3		V-70	30	48	59	13500	1.63
4	BES	AIBN	60	24	88	4100	1.94
5		AIBN	45	48	67	6500	2.40
6		V-70	30	48	67	8800	5.58
7	IPES	AIBN	60	24	[f]	[f]	[f]
8		AIBN	45	24	63	3000	1.29
9[g]	PES	AIBN	60	24	5	2800	1.42

[a] Bulk polymerization at $[M]_0/[I]_0 = 100$. [b] NES = neopentyl ethenesulfonate, BES = 1-butyl ethenesulfonate, IPES = isopropyl ethenesulfonate, and PES = phenyl ethenesulfonate. [c] AIBN = 2,2′-azobis(isobutyronitrile), and V-70 = 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile). [d] Calculated by ^{1}H NMR in $CDCl_3$. [e] Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF. [f] Insoluble in $CDCl_3$ and THF. [g] Solvent = chlorobenzene ([M] = 1.0 g/mL).

SEC chromatograms of the poly(vinyl sulfonate ester)s were obtained in DMF containing 10 mM LiBr at 40 °C at a flow rate of 1.0 mL/min with a Tosoh HPLC HLC-8220 system. The column set was as follows: four consecutive 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].

Results and Discussion

Screening of Reaction Conditions. In this study, we focused on the radical polymerization of vinyl sulfonate esters having different substituent groups, neopentyl ethenesulfonate (NES), 1-butyl ethenesulfonate (BES), isopropyl ethenesulfonate (IPES), and phenyl ethenesulfonate (PES), as shown in Scheme 1. Different from styrene, (meth)acrylate, and (meth)acrylamide-type monomers, the direct linkage of the sulfonate moiety 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. Three vinyl sulfonate esters having different substituent groups (NES, BES, and IPES) were synthesized by the reaction of 2-chloroethanesulfonyl chloride with corresponding alcohols according to a previously reported method with slight modifications (Scheme 1).[33,45,46] NES, BES, and IPES were liquid at room temperature, whereas commercial PES was employed as a solid monomer.

Initially, we compared the conventional radical polymerization of four vinyl sulfonate esters having different substituent groups, in order to find conditions for obtaining polymeric product having relatively high molecular weight with sufficient yield. Bulk polymerization of the vinyl sulfonate esters was conducted at $[M]_0/[I]_0 = 100$ under various conditions. The results are summarized in Table 1. When the bulk polymerization of NES was conducted with AIBN at 60 °C, the polymer having relatively low molecular weight ($M_n = 5000$, $M_w/M_n = 2.04$) was obtained with high monomer conversion (>90%, as determined by ^{1}H NMR spectroscopy) after 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 polymerization time. The polymerization at lower temperature led to the decrease in polymer yield with the formation of the higher molecular weight products ($M_n = 8300$, $M_w/M_n = 1.98$ at 45 °C with AIBN, and $M_n = 13500$, $M_w/M_n = 1.63$ at 30 °C with V-70). The same tendency was observed in the polymerization of BES (see Figures S5 and S6, Supporting Information), indicating a negligible effect of the bulkiness of the primary alkyl group on the reactivity of the vinyl group. In the cases of the free radical polymerization of IPES in bulk, the insoluble product was obtained at 60 °C, whereas a polymer having relatively low molecular weight ($M_n = 3000$, $M_w/M_n = 1.29$) was obtained at 45 °C. Since PES was a solid monomer, the polymerization of PES was conducted in chlorobenzene at 60 °C. Unfortunately, the monomer conversion was extremely low (5%), suggesting the insufficient reactivity of PES.

The ^{1}H NMR chemical shifts of vinyl groups of monomers were reported to be correlated with the reactivities of monomers.[48,49] The comparison of chemical shifts of vinyl groups of the monomers evaluated by ^{1}H and ^{13}C NMR spectroscopy (Supporting Information, Figures S7 and S8) supported the different reactivities of primary alkyl vinyl sulfonate (NES and BES), compared with those of the other two vinyl sulfonate esters (IPES and PES). These results suggest that the different substituent groups on the sulfonate ester moiety have significant influence on the reactivity of the vinyl group in these monomers. In contrast, no significant difference on the chemical shift was detected between NES and BES. The relatively low molecular weights of poly(vinyl sulfonate ester) derivatives could account for an inherent tendency of the propagating radical to undergo chain transfer reactions. On the basis of these preliminary results, we selected NES and BES for our further investigations toward the precise synthesis of poly(vinyl sulfonate ester)s having low polydispersity and controlled molecular weights.

RAFT Polymerization. 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-methoxycarbonyl) ethyldithiocarbonate (CTA 4), and *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 5), were selected as CTAs (Scheme 2). The recent progress of the RAFT/MADIX (macromolecular design via the interchange of xanthates) process 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, such as vinyl acetate,[50−52] *N*-vinylpyrrolidone,[52−56] *N*-vinylcarbazole,[39,57,58] *N*-vinylindole,[40] and *N*-vinylphthalimide.[43] We also employed dithiobenzoate-type CTA (CTA 1) and dithiocarbamate-type CTA (CTA 2) 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.[59−62] 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).[63] Dithiocarbamate-type CTA 2, in which a nitrogen lone pair is part of an aromatic ring system, has been employed for the RAFT polymerizations of conventional conjugated monomers, such as styrene,[37,64] methyl

Table 2. Bulk Polymerization of Neopentyl Ethenesulfonate (NES) and 1-Butyl Ethenesulfonate (BES) with 2,2′-Azobis(isobutyronitrile) (AIBN) Using Different Chain Transfer Agents (CTAs) in Bulk at 60 °C for 24 h[a]

entry	monomer	CTA[b]	conv.[c] %	M_n[d] (theory)	M_n[e] (SEC)	M_w/M_n[e] (SEC)
1	NES	CTA 1	< 5			
2		CTA 2	22	2200	1300	1.18
3		CTA 3	20	2000	1200	1.14
4		CTA 4	88	8100	3300	1.41
5		CTA 5	18	1800	1800	1.20
6	BES	CTA 1	0			
7		CTA 2	18	1700	1800	1.17
8		CTA 3	26	2300	2200	1.26
9		CTA 4	86	7300	3300	1.48
10		CTA 5	12	1200	1400	1.18

[a] $[M]_0/[CTA]_0/[AIBN]_0$ = 100/2/1. [b] CTA 1 = benzyl dithiobenzoate, CTA 2 = benzyl 1-pyrrolecarbodithioate, CTA 3 = *S*-benzyl-*O*-ethyl dithiocarbonate, CTA 4 = *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate, and CTA 5 = *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate; see Scheme 2. [c] Calculated by ^{1}H NMR in $CDCl_3$. [d] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of M) × $[M]_0/[CTA]_0$ × conv. + (MW of CTA). [e] Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF.

acrylate,[64] *N*-isopropylacrylamide,[65] as well as less active monomers involving *N*-vinylphthalimide[43] and *N*-vinylnaphthalimide[66]

The polymerization of NES was conducted in bulk with different CTAs and AIBN as an initiator at 60 °C for 24 h at $[M]_0/[CTA]_0 = 50$ using the ratio of AIBN to CTA of 1:2 ($[M]_0/[CTA]_0/[AIBN]_0 = 100/2/1$). The results are summarized in Table 2. When the polymerization was carried out using CTA 4, a poly(NES) having a relatively low polydispersity ($M_w/M_n = 1.41$) was obtained with a high conversion (88%, as determined by ^{1}H NMR spectroscopy). As shown in Figure 1a, a unimodal SEC peak with a slight tailing peak at the low molecular weight region is detected in the SEC chart of the poly(NES) obtained with CTA 4. RAFT polymerizations of NES with CTA 2, CTA 3, and CTA 5 afforded poly(NES)s having low molecular weights and narrow molecular weight distributions (M_n = 1200−1800 g/mol, M_w/M_n = 1.14−1.20) with relatively low monomer conversions (< 25%). Several peaks corresponding to oligomers were detected at the low molecular weight region in the SEC traces of the resulting polymers (see Figure S9 in Supporting Information). Extremely low monomer conversion (< 10%) was obtained for the polymerization with CTA 1 under the same conditions. These results suggest that the xanthate-type CTA 4 is efficient for RAFT polymerizations of NES.

The behavior is consistent with the general tendency, in which the transfer constants decrease in the series where Z is phenyl ≫ pyrrole ≫ alkoxy.[67] In other words, the transfer constants of the dithiobenzoate-type CTA 1 and dithiocarbamate-type CTA 2 are too high, resulting in low monomer conversions. These results also support the idea that the reactivity of the propagating vinyl sulfonate radical is comparable to that of *O*- and *N*-vinyl nonconjugated monomers having electron-donating properties. Similar to typical nonconjugated monomers, the propagating radical of the vinyl sulfonate ester is relatively unstable and is a poor homolytic leaving group, even if the vinyl group is directly connected to the electron-withdrawing sulfonate group in the monomer. As shown in Scheme 3, xanthate-type CTA increases the electron density at the radical center, which may lead to the destabilization of the intermediate radicals and an increase in the fragmentation rate. The electron-donating *O*-alkyl substituent may lead to stabilization of the polymeric thiocarbonylthio product through their conjugation with the C=S double bond, which lowers the rate of addition of the propagating radicals to the sulfur atom. Consequently, a delicate balance of the forward and reverse rates of addition and fragmentation can be obtained. Hence, unfavorable chain transfer and termination reactions due to the high reactivity of the propagating radicals derived from the vinyl sulfonate ester could be suppressed by the MADIX/RAFT process using the xanthate-type CTA.

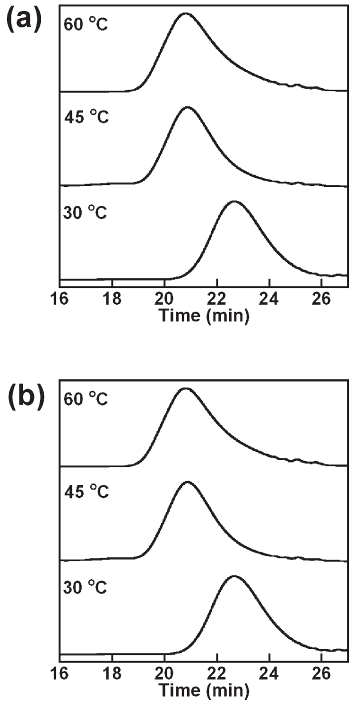
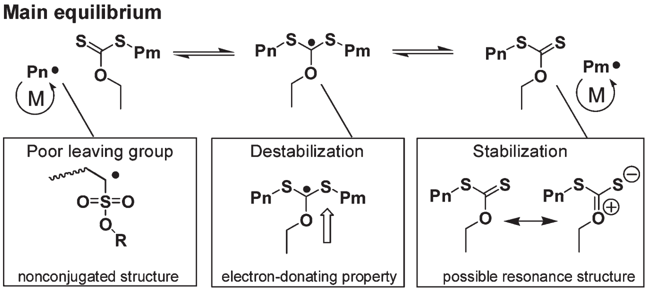


Figure 1. SEC traces (THF) of (a) poly(NES)s and (b) poly(BES)s obtained by RAFT polymerizations with CTA 4 at different temperatures. See Table 3 for detailed polymerization conditions.

Scheme 3. Proposed Mechanism of Xanthate-Mediated Controlled Radical Polymerization of Vinyl Sulfonate Ester



The same tendency was observed in RAFT polymerizations of BES with different CTAs. When the polymerization was carried out using CTA 4 at 60 °C, a polymer showing a monomodal SEC peak (M_w/M_n = 1.48, Figure 1b) was obtained with a sufficient conversion (86%). In contrast, the polymerizations with CTA 2, CTA 3, and CTA 5 afforded poly(BES)s having low molecular weights (M_w/M_n = 1.17−1.26, M_n = 1400−2200 g/mol) with low monomer conversions (< 30%). SEC traces of the poly(BES)s obtained under the conditions showed several peaks corresponding to oligomers (see Figure S10 in Supporting Information). It was reported that steric 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.[68] The secondary radicals, produced from CTA 4 and CTA 5, are more easily formed

Table 3. Effects of Temperature and Initiator on RAFT Polymerization of Neopentyl Ethenesulfonate (NES) and 1-Butyl Ethenesulfonate (BES) with CTA 4[a]

entry	monomer	initiator	temp (°C)	time (h)	conv.[b] %	M_n[c] (theory)	M_n[d] (SEC)	M_w/M_n[d] (SEC)
1	NES	AIBN	60	24	88	8100	3300	1.41
2		AIBN	45	48	78	7200	3900	1.34
3		V-70	30	48	54	5000	3900	1.19
4	BES	AIBN	60	24	70	6000	2400	1.50
5		AIBN	45	48	57	4900	2800	1.29
6		V-70	30	48	68	5800	3300	1.31

[a] $[I]_0/[CTA\ 4]_0/[M]_0 = 1/2/100$, AIBN = 2,2′-azobis(isobutyronitrile), V-70 = 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), and CTA 4 = *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate. [b] Calculated by ^{1}H NMR in $CDCl_3$. [c] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of M) × $[M]_0/[CTA\ 4]_0$ × conv. + (MW of CTA). [d] Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF.

than the primary benzyl radical expelled from CTA 3, resulting in the faster consumption of CTA and uniform initiation. The transfer constant ($C_{tr} = k_{tr}/k_p$) of CTA 4 was reported to be 0.89 for the bulk polymerization of styrene, which was comparable to that of CTA 5 (C_{tr} = 0.82).[69] Among xanthate-type CTAs, CTA 4 may show 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 that RAFT/MADIX polymerization utilizing *O*-alkyl xanthates as CTAs is a very efficient method to control the polymerization of highly reactive propagating radicals derived from the vinyl sulfonate ester.

In the next stage, we examined the influences of the polymerization temperature and initiator in terms of the monomer conversion, molecular weights, and the polydispersity of the resulting poly(NES) and poly(BES). The polymerization was conducted with the xanthate-type CTA 4 at low temperatures (45 °C with AIBN and 30 °C with V-70) for 48 h at a constant monomer/chain transfer agent/initiator ratio ($[M]_0/[CTA]_0/[I]_0 = 100/2/1$). The results are summarized in Tables 3. When the RAFT polymerization of NES was conducted at 45 °C at $[NES]_0/[CTA\ 4]_0/[AIBN]_0 = 100/2/1$, the polymer having a relatively low polydispersity ($M_w/M_n = 1.34$) was obtained with a sufficient conversion (conv. = 78%). A low polydispersity product ($M_w/M_n = 1.19$) was obtained by RAFT polymerization with V-70 at 30 °C under the same conditions. This behavior can be also explained by the assumption that decreasing the temperature leads to a decrease in the radical reactivity, resulting in the increased selectivity of the various radical reactions to minimize unfavorable side reactions. Another possible explanation is that the lower polymerization temperature causes a remarkable decrease of the fragmentation rate constant, leading to the decreased number of the active propagating radical. In the cases of the polymerizations of BES, the polymers having relatively low polydispersities (M_w/M_n = 1.29−1.31) with moderate conversions (57−68%) were obtained at $[BES]_0/[CTA\ 4]_0/[I]_0 = 100/2/1$ in both polymerization systems (45 °C with AIBN and 30 °C with V-70). Narrow unimodal SEC peaks (M_w/M_n = 1.29−1.31) are seen in the SEC charts of the poly(BES)s obtained under the conditions described (Figure 1b).

The RAFT polymerization of NES and BES was also conducted at higher chain transfer agent/initiator ratio ($[CTA\ 4]_0/[I]_0 = 5/1$), and the results are summarized in Table S2 (see Supporting Information). When the polymerization of NES was carried out with CTA 4 and AIBN at 45 °C, the monomer conversion decreased from 78% to 16% as the $[CTA]_0/[AIBN]_0$ ratio increased from 2 to 5, indicating significant influence of the CTA/initiator ratio on the monomer conversion. The poly(NES) having low polydispersity ($M_w/M_n = 1.14$, $M_n = 1500$) was obtained at higher $[CTA]_0/[AIBN]_0$ ratio ($[M]_0/[CTA\ 4]_0/[I]_0 = 250/5/1$). At 45 °C, the polymerization of BES at $[CTA]_0/[AIBN]_0 = 5$ also led to the formation of poly(BES) having narrower molecular weight distribution with a slight decrease in the monomer conversion (conv. = 54%, $M_w/M_n = 1.23$, M_n = 3500 g/mol). 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 because of a decrease in the number of radicals available for unfavorable side reactions but result in longer polymerization time. In contrast, no significant influence of the $[CTA]_0/[I]_0$ ratio on the monomer conversion, molecular weights, and the polydispersity of the resulting polymers was observed in the polymerization with V-70 at 30 °C.

Control of Molecular Weights. With a view of preparing poly(vinyl sulfonate ester)s over a wide range of molar mass, different degrees of polymerization were targeted. For this purpose, the polymerization of two vinyl sulfonate esters (NES and BES) was conducted at different $[M]_0/[CTA\ 4]_0$ ratios between 25 and 200, while the AIBN/CTA molar ratio was held constant at 1/2. The results are shown in Table 4. When the polymerizations of NES were conducted in bulk at 45 °C for 72 h, the conversions were nearly 67−83% (determined by ^{1}H NMR spectroscopy). The number-average molecular weights of the poly(NES)s increase with the $[M]_0/[CTA]_0$ ratio, and the molecular weight distributions remain narrow (M_w/M_n = 1.22−1.30) until $[M]_0/[CTA]_0$ = 100, indicating the feasibility of controlling the molecular weights. In the cases of the polymerizations at $[M]_0/[CTA]_0$ = 25−100, the SEC traces are unimodal with no evidence of high molecular weight species, as shown in Figure 2a. When the polymerizations of BES were conducted with CTA 4 under the same conditions, the same tendency was observed in terms of the molecular weight controlled by the monomer/CTA molar ratio with maintaining relatively low polydispersity. A shift in the SEC trace toward higher molecular weight regions with unimodal peaks is seen with increasing $[M]_0/[CTA]_0$ ratio (Figure 2b), demonstrating the efficient control of the molecular weights. In both cases, the relatively higher molecular weight products obtained at $[M]_0/[CTA]_0$ = 200 (entries 4 and 8 in Table 4) lead to broader polydispersities. This may be due to the relatively high molecular weight of the resulting product with increased viscosity during the bulk polymerization. The polymerization of NES using V-70 at lower temperature (30 °C) was also investigated at $[M]_0/[CTA]_0$ = 25−200. As can be seen in Figure 3 and Table S3 (Supporting Information), the increase in the $[M]_0/[CTA]_0$ ratio leads to a clear shift in the SEC trace toward higher molecular weight regions. In contrast, an apparent broadening of the molar mass distribution is observed for the products obtained at higher $[M]_0/[CTA]_0$ ratios, suggesting that the controlled character of the polymerization of NES using V-70 at a lower temperature (30 °C) is comparable to that with AIBN at 45 °C. Nevertheless,

Table 4. RAFT Polymerization of Neopentyl Ethenesulfonate (NES) and 1-Butyl Ethenesulfonate (BES) with 2,2′-Azobis(isobutyronitrile) (AIBN) and CTA 4 at Different [M]/[CTA] Ratios in Bulk at 45 °C for 72 h[a]

entry	monomer	$[M]_0$ /$[CTA\ 4]_0$	conv.[b] %	M_n[c] (theory)	M_n[b] (NMR)	M_n[d] SEC (THF/DMF)	M_w/M_n[d] SEC (THF/DMF)
1	NES	25	83	3900		3200/2800	1.22/1.35
2		50	78	7200		5200/4400	1.26/1.44
3		100	67	12200	14600 [e]	7400/6100	1.30/1.51
4		200	73	26200		10100/8800	1.53/1.61
5	BES	25	80	3500	7300	2900/9400	1.24/1.23
6		50	77	6500	13400	4100/13600	1.39/1.29
7		100	71	11900	21400	5200/16500	1.45/1.45
8		200	62	20600	37700	7400/20200	1.47/1.44

[a] $[CTA\ 4]_0/[AIBN]_0 = 2$, and CTA 4 = *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate. [b] Calculated by ^1H NMR in $CDCl_3$. [c] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of M) × $[M]_0/[CTA]_0$ × conv. + (MW of CTA). [d] Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF and DMF (0.01 M LiBr). [e] The sample purified by dialysis was employed for ^1H NMR measurement.

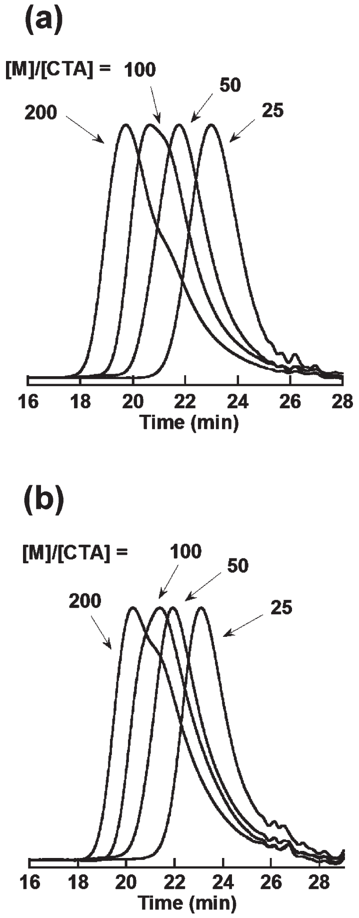


Figure 2. SEC traces (THF) of (a) poly(NES)s and (b) poly(BES)s obtained by RAFT polymerization with AIBN and CTA 4 at different [M]/[CTA] ratios; CTA 4 = *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate, AIBN = 2,2′-azobis(isobutyronitrile), and polymerization temperature = 45 °C. See Table 4 for detailed polymerization conditions.

these results suggest that the molecular weights of poly(vinyl sulfonate ester)s can be easily adjusted by the monomer-to-CTA ratio and that the polymers having relatively low polydispersities can be obtained by RAFT polymerization of the vinyl sulfonate esters under suitable conditions.

In all cases, the experimental molecular weights determined by conventional GPC in THF are lower than the theoretical ones. These discrepancies are believed to result from the difference in hydrodynamic volume between poly(vinyl sulfonate ester)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 absolute molecular weights of poly(NES) and poly(BES). The CTA-derived initiator may produce the polymer with CTA fragments at the polymer chain ends (α-chain end with the (1-methoxycarbonyl) ethyl group and ω-chain end with the dithiocarbonate group in the case of CTA 4). The ^1H NMR spectrum of the poly(NES) obtained at $[NES]_0/[CTA\ 4]_0/[AIBN]_0 = 200/2/1$, followed by the purification via dialysis, is presented in Figure 4a. The characteristic peaks at 4.2−3.8 (CH_2-$C(CH_3)_3$), 4.2−3.2 (CH in the polymer main chain), 2.8−1.6 (CH_2 in the polymer main chain), 1.2−0.8 (CH_2−$C(CH_3)_3$) ppm are clearly seen, which are attributed to the poly(NES) main chain. In addition to these peaks, methylene protons are clearly visible at 4.8−4.6 ppm, which correspond to the ethoxy fragment at the dithiocarbonate chain end of the polymer. 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 peaks for the chain-end protons to those of the main-chain protons. The molecular weight of poly(NES) prepared with CTA 4 can be calculated by comparison of the area of the peak at 1.2−0.8 ppm corresponding to the methyl protons (9H) of the neopentyl group (peak d in Figure 4a) in NES repeating units to the peak at 4.8−4.6 ppm (peak e) corresponding to the methylene protons (2H) of the ethoxy end group. The chain-end structures were also detected in the poly(BES) obtained with CTA 4, followed by purification via decantation (Figure 4b). As shown in Table 4, the molecular weights determined by NMR are comparable to the theoretical values calculated using eq 1, which are

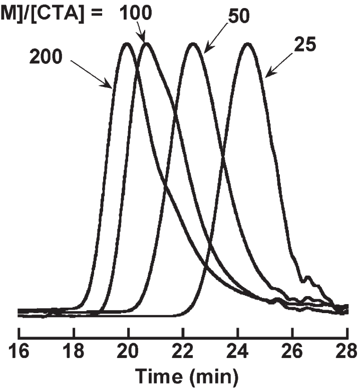


Figure 3. SEC traces (THF) of poly(NES)s obtained by RAFT polymerization with V-70 and CTA 4 at different [M]/[CTA] ratios; CTA 4 = *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate, V-70 = 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), and polymerization temperature = 30 °C. See Table S3 (Supporting Information) for detailed polymerization conditions.

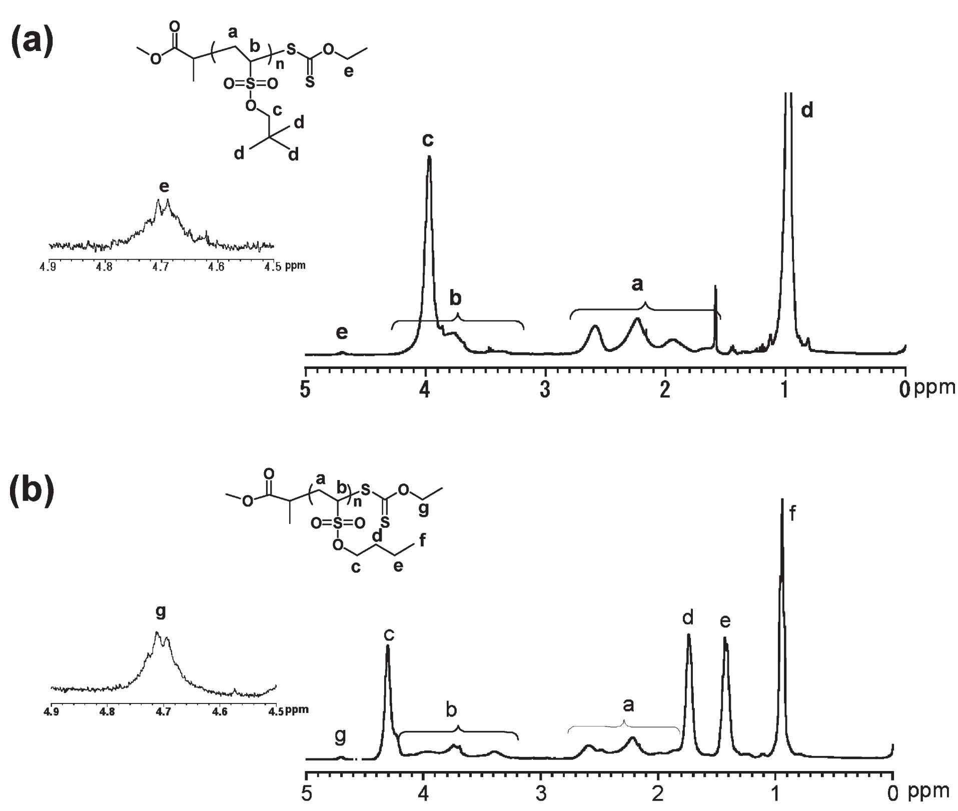


Figure 4. ^{1}H NMR spectra (CDCl$_3$) of (a) poly(NES) and (b) poly(BES) prepared by the polymerization with CTA 4 obtained at [NES]$_0$/[CTA 4]$_0$/[AIBN]$_0$ = 200/2/1. See Table 4 for detailed polymerization conditions.

apparently higher than those obtained from SEC in THF using polystyrene standards. The molecular weights of poly(BES)s determined by SEC in DMF (0.01 M LiBr) are also comparable to the theoretical values (see Figure S11 in Supporting Information).

Polymerization Kinetics. The controlled/living character of the polymerization of two vinyl sulfonate esters, NES and BES, was studied by performing kinetics investigations in the presence of CTA 4 with AIBN at 45 °C. The results are shown in Figure 5. When the reaction was conducted at [NES]$_0$/[CTA]$_0$/[AIBN]$_0$ = 100/2/1, a relatively high conversion (78%) was reached after 48 h. An almost linear first-order kinetic plot is seen under the conditions (Figure 5a). As shown in Figure 5b, a linear increase in the number-average molecular weight with conversion suggests a constant number of propagating chains throughout the polymerization. The SEC traces (THF) of poly(NES)s obtained at different reaction times are shown in Figure 5c. A progressive increase in the molar mass with conversion with narrow unimodal SEC peaks (M_w/M_n = 1.17−1.34) is evident and typical for a controlled polymerization. Note that no shoulder peak at high molecular weight region appears even at the last stage of the polymerization, suggesting the absence of the termination reaction due to the combination of the growing polymer chains during a longer reaction time. The peaks corresponding to oligomers were detected at the low molecular weight region in the SEC traces of the polymers obtained at the initial stage of the polymerization, regardless of NES and BES. In the case of the polymerization of BES, the polymerization rate is slightly slower than that of NES. Nevertheless, a linear increase in the number-average molecular weights, M_n, with conversion is seen in the polymerization of BES, and the polydispersity indices (M_w/M_n) for all samples ranging between 1.17 and 1.32 (Figure 5e). The SEC traces of poly(BES) obtained at different polymerization times illustrate the increase in molar mass with time. Symmetrical unimodal SEC peaks without shoulders and tailings are seen for the poly(BES)s up to about 60% conversion, as can be seen in Figure 5f.

Chain Extension. 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 investigate this point, the dithiocarbonate-terminated poly(NES) ($M_{n,SEC}$ = 5700 g/mol, M_w/M_n = 1.09) prepared by the polymerization using CTA 4 at the ratio [NES]$_0$/[CTA 4]$_0$/[AIBN]$_0$ = 250/5/1, followed by the purification via dialysis, was employed as a macro-CTA for the chain extension experiment. The chain extension was performed at 45 °C for 48 h at the ratio [NES]$_0$/[macro-CTA]$_0$/[AIBN]$_0$ = 100/2/1 in chlorobenzene (monomer concentration = 1.0 g/mL). After the chain extension, the resulting product was analyzed by SEC in THF and compared to the original macro-CTA. As can be seen in Figure 6, a clear shift in the SEC trace toward the higher molecular weight region is seen after the chain extension. The extended polymer exhibited a SEC peak with a relatively low polydispersity (M_w/M_n = 1.37) with a tailing peak at the low molecular weight region. These results suggest that a small amount of residual low molecular weight dead chains remains in the final product. Further investigations are required to achieve the poly(NES), which are fully functionalized with the dithiocarbonate end group and can be used as a macro-CTA for further chain extension reactions.

Synthesis of Block Copolymers. For the synthesis of well-defined block copolymers containing the poly(vinyl sulfonate ester) segment, we selected poly(*N*-vinylcarbazole), poly(NVC), as a hydrophobic segment. Initially, we conducted the synthesis of a block copolymer by RAFT polymerization of NES using poly(NVC) as a macro-CTA, as shown in Scheme 4. For the synthesis of well-defined block

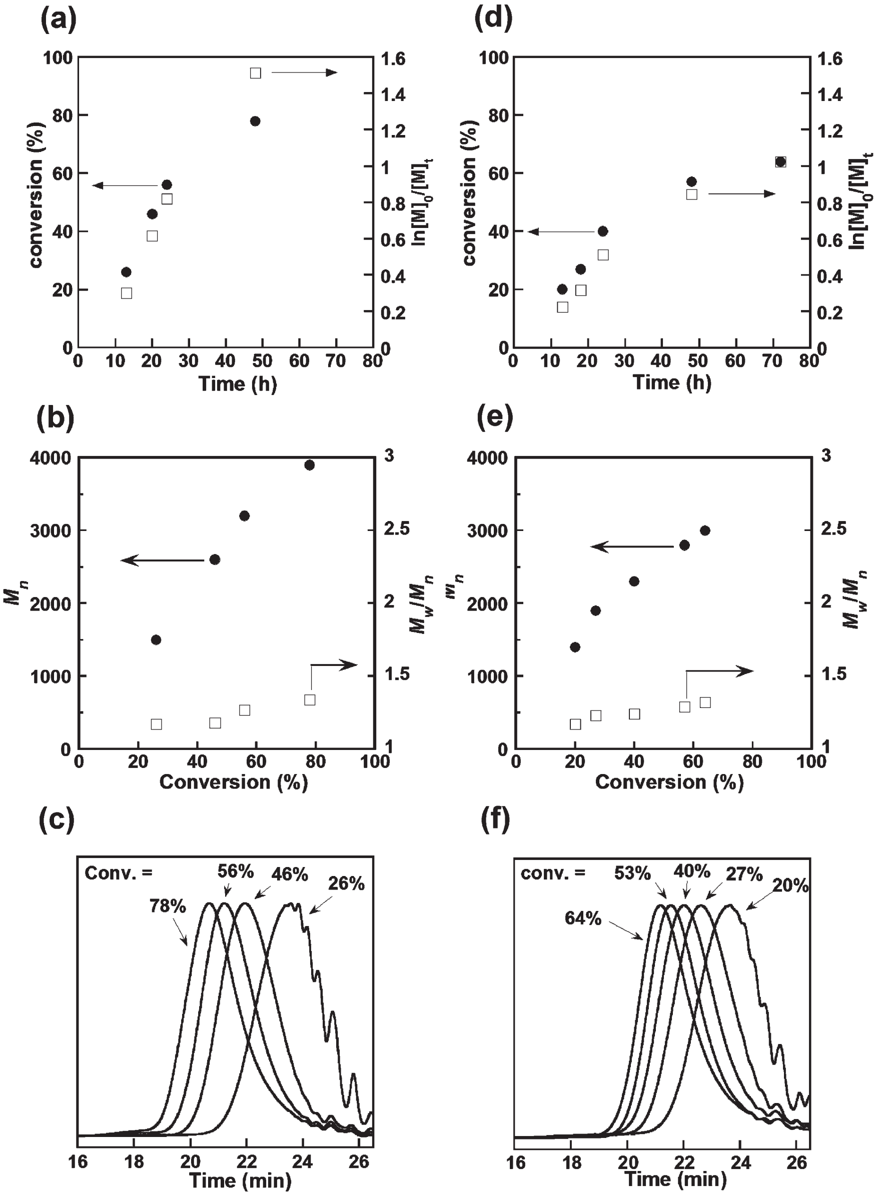


Figure 5. (a,d) Time–conversion (circles) and first-order kinetic (squares) plots for the polymerization of neopentyl ethenesulfonate (a–c; NES) and 1-butyl ethenesulfonate (d–f; BES), with 2,2′-azobis(isobutyronitrile) (AIBN) in the presence of *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate (CTA 4) in bulk at 45 °C at $[M]_0/[CTA]_0/[AIBN]_0 = 100/2/1$. (b,e) Number-average molecular weight (circles) and polydispersity (squares) as a function of conversion. (c,f) Evolution of SEC traces (THF) of the products with conversion.

copolymers by the RAFT process, the order of blocking is crucial. In this case, the first xanthate-terminated poly(NVC) should have a high transfer constant in the subsequent polymerization of the second monomer, NES, to give the second block.[70,71] In order to achieve the block copolymer with low polydispersity, additionally, 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. The xanthate-terminated poly(NVC) having low molecular weight was initially prepared by RAFT polymerization with CTA 4. The polymerization of NES was conducted in the presence of the xanthate-terminated poly(NVC) at $[NES]_0/[macro\text{-}CTA]_0/[AIBN]_0 = 200/2/1$ in chlorobenzene at 60 °C for 24 h. Figure 7 shows the SEC traces of the parent poly(NVC) and resulting product. A shift of the SEC trace toward the higher molecular weight region, with polydispersity remaining $M_w/M_n = 1.21$, clearly demonstrates efficient block formation.

The ^{1}H NMR spectrum of the block polymer, poly(NVC)-*b*-poly(NES), is shown in Figure 8a. The peaks corresponding to poly(NVC) and poly(NES) are clearly observed in the spectrum measured in $CDCl_3$. Integration of the appropriate peaks gave the comonomer composition (NVC:NES = 79:21). The molecular weight of the block copolymer ($M_{n,NMR} = 4300$) evaluated from the composition determined by ^{1}HNMR and the molecular weight of the poly(NVC) macro-CTA is comparable to the value observed by SEC ($M_{n,SEC} = 4400$). These results clearly demonstrate that the chain extension from the poly(NVC) macro-CTA to NES can be well controlled and provides the block copolymer with the as-designed chain structure and narrow molecular weight distribution.

We also attempted to synthesize the block copolymer by RAFT polymerization of NVC using poly(NES) as a macro-CTA. However, this attempt was unsuccessful. As shown in Figure S12 (see Supporting Information), the SEC chromatogram of the product showed bimodal distributions, which may be attributed to the residue of the starting poly(NES) macro-CTA and second-growth polymer, suggesting insufficient blocking efficiency and/or the existence of a small number of dead chains. These results suggest that the first xanthate-terminated poly(NES) (S = C(Z)S-A; A block corresponds to poly(NES), whereas Z is the dithiocarbonate group) has an insufficient transfer constant in the subsequent polymerization of NVC. This is an indication that the leaving ability of propagating poly(NES) radical (A•) is lower than that of the second poly(NVC) radical (B•) under the reaction conditions. Another attempt to synthesize the block copolymer by RAFT polymerization of NES using poly(BES) as a macro-CTA was also unsuccessful. Bimodal distributions in the SEC chromatogram of the product (Figure S13, see Supporting Information) suggest insufficient blocking efficiency and/or the existence of a small number of dead chains. Further studies to achieve various types of block copolymers containing poly(vinyl sulfonate ester)s are now in progress.

Deprotection of Poly(NES). Deprotection of the neopentyl group in poly(NES) was achieved using LiBr in refluxing 2-butanone (Scheme 5) according to a previously reported procedure with slight modifications.[47] Quantitative deprotection was confirmed by ^{1}H NMR measurements of the samples obtained by the treatment. As can be seen in Figure 9, complete disappearance of the peak corresponding to the neopentyl resonance between 0.8 and 1.2 ppm is observed clearly. We also conducted FT-IR measurements of poly(NES) before and after the deprotection (Figure 10). The absorption at 1167 and 1350 cm^{-1} corresponding to a typical sulfonate ester disappears, whereas the absorption at 1052 and 1194 cm^{-1} corresponding to a sulfonate salt is observed after the treatment. FT-IR spectrum of the deprotected sample is almost the same as that of poly(sodium vinyl sulfonate) prepared by conventional radical polymerization of sodium vinyl sulfonate. The resulting poly(lithium vinyl sulfonate) was soluble in water, while insoluble in MeOH, DMSO, DMF, THF, and $CHCl_3$. The thermal stabilities of the resulting polymers were evaluated by thermogravimetric analysis (TGA) under nitrogen (Figure S14, see Supporting Information). Poly(NES) lost about 30% weight around 130−140 °C, and then the second mass-loss region at 150−300 °C was clearly observed. Poly(lithium vinyl sulfonate) was stable until 330 °C, and then the thermal degradation started. The temperatures for 10% weight loss of poly(lithium vinyl sulfonate) and poly(NVC)-*b*-poly(lithium vinyl sulfonate) under nitrogen atmosphere were 340 and 330 °C, respectively.

The deprotection of the neopentyl group in the block copolymer, poly(NVC)-*b*-poly(NES), was carried out under

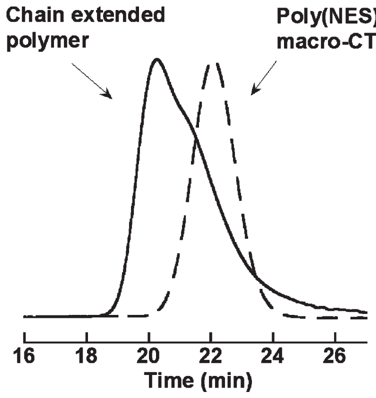


Figure 6. SEC traces of the parent poly(NES) macro-CTA (dotted line, $M_{n,SEC}$ = 5700 g/mol, M_w/M_n = 1.09) obtained with CTA 4 at 45 °C for 48 h and the chain extended polymer (solid line, M_n = 8000 g/mol, M_w/M_n = 1.37) obtained after the polymerization of NES in chlorobenzene (monomer concentration = 1.0 g/mL) at 45 °C at the ratio $[NES]_0/[macro\text{-}CTA]_0/[AIBN]_0$ = 100/2/1 for 48 h.

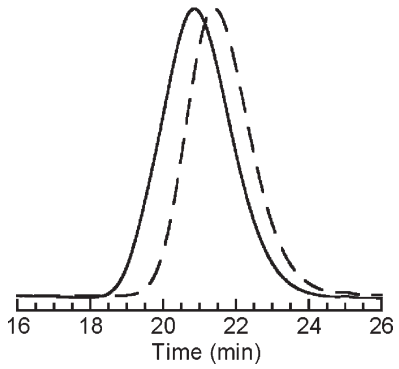


Figure 7. SEC traces of poly(NVC) macro-CTA (dotted line, M_n = 3400, M_w/M_n = 1.16) and the product obtained by the polymerization of NES (solid line, M_n = 4400, M_w/M_n = 1.21).

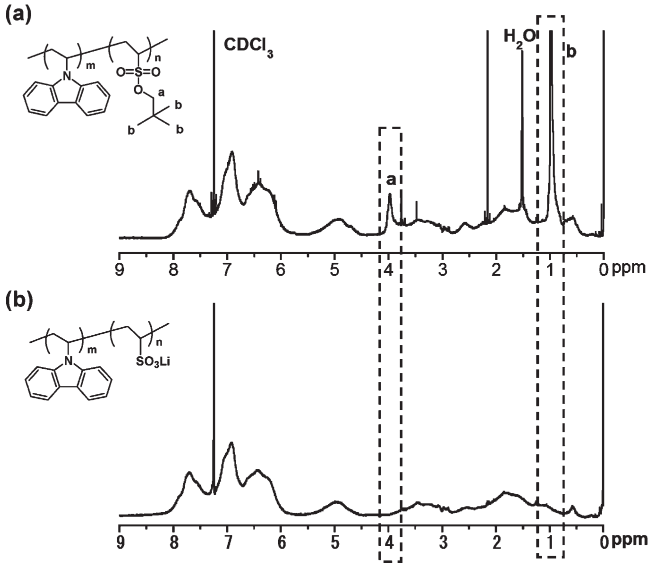
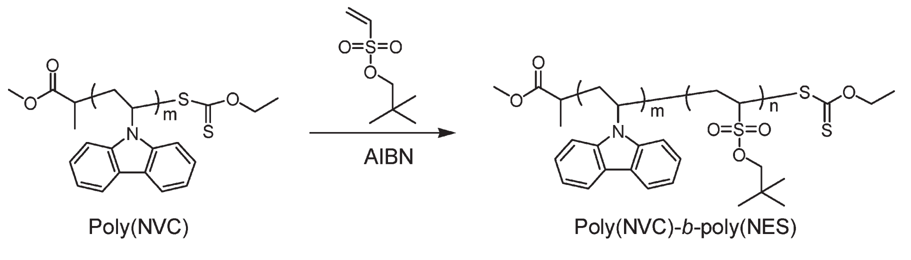


Figure 8. ^{1}H NMR spectra of (a) poly(NVC)-*b*-poly(NES) and (b) poly(NVC)-*b*-poly(lithium vinyl sulfonate) in $CDCl_3$.

Scheme 4. Synthesis of Block Copolymer by Polymerization of NES Using Poly(NVC) As Macro-CTA



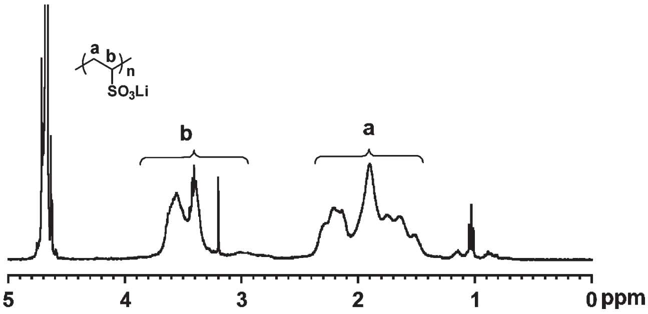


Figure 9. ^{1}H NMR spectrum of poly(lithium vinyl sulfonate) in D_2O.

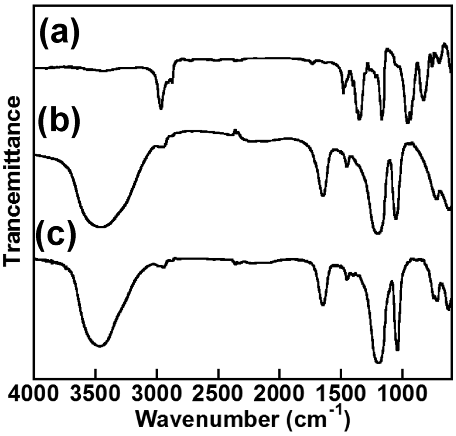
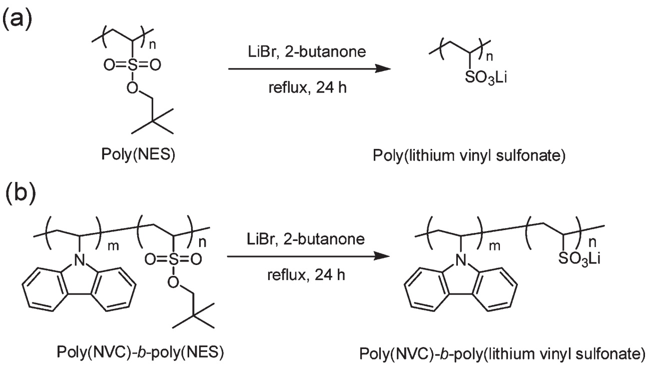


Figure 10. FT-IR spectra of (a) poly(NES), (b) poly(lithium vinyl sulfonate) obtained by RAFT polymerization of NES, followed by deprotection, and (c) poly(sodium vinyl sulfonate) prepared by conventional radical polymerization of sodium vinyl sulfonate.

Scheme 5. Synthesis of (a) Poly(lithium vinyl sulfonate) and (b) Poly (*N*-vinylcarbazole)-*b*-poly(lithium vinylsulfonate) by Deprotection



the same conditions. The ^{1}H NMR spectrum of the resulting product obtained after the deprotection shows the complete disappearance of the peak at 0.8−1.2 ppm corresponding to the neopentyl group (Figure 8b). The resulting product can be regarded as an amphiphilic block copolymer comprising poly(lithium vinyl sulfonate) as a strong anionic polyelectrolyte and poly(NVC) as a hydrophobic segment. Further studies on the properties and the assembled structures of the block copolymers having different composition and chain length are now in progress, which will be separately reported.

Conclusions

This work presents the synthesis of well-defined polymers with pendant sulfonate esters and lithium sulfonate groups by RAFT polymerization of vinyl sulfonate esters using the xanthate-type mediating agent, CTA 4. The controlled character of the polymerization of two vinyl sulfonate esters having primary alkyl groups, NES and BES, was confirmed, and there was no significant difference in the polymerization behavior between NES and BES. The dithiocarbonate end-capped poly(NVC) was employed as a macro-CTA for the synthesis of the block copolymer, poly(NVC)-*b*-poly(NES), having low polydispersity. Deprotection of the neopentyl group of the poly(NES) and poly(NVC)-*b*-poly(NES) proceeded smoothly to give well-defined poly(lithium vinyl sulfonate) and poly(NVC)-*b*-poly(lithium vinyl sulfonate), respectively. We believe that this article represents the first report on controlled radical polymerization of the vinyl sulfonate esters via RAFT and the synthesis of well-defined poly(lithium vinyl sulfonate) and its block copolymer. This work substantially broadens and extends the scope of sulfonic acid-containing polymers, in which precise control of the molecular weight, polydispersity, topology, composition, and functions can be achieved using a controlled radical polymerization technique.

Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of four vinyl sulfonate esters, GPC traces of poly(vinyl sulfonate ester)s prepared under different conditions, the products obtained by the polymerization of NVC using poly(NES) macro-CTA, the polymerization of NES using poly(BES) macro-CTA, and TGA thermograms of poly(NES), poly(lithium vinyl sulfonate), and sulfonated block copolymer, and tables summarizing the solubility of the products and data of the polymerization at $[M]_0/[\text{CTA } 4]_0/[I]_0 = 250/5/1$. This material is available free of charge via the Internet at http://pubs.acs.org.

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