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RAFT Polymerization of *N*-Vinylimidazolium Salts and Synthesis of Thermoresponsive Ionic Liquid Block Copolymers

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ABSTRACT: The polymerizations of *N*-vinylimidazolium salts, 1-(3-phenylpropyl)-3-vinylimidazolium bromide (PVI-Br), 1-(6-ethoxycarbonylhexyl)-3-vinylimidazolium bromide (EHVI-Br), and 1-(2-ethoxyethyl)-3-vinylimidazolium bromide (EtOEVI-Br), were performed by reversible addition−fragmentation chain transfer (RAFT)/macromolecular design via interchange of xanthate (MADIX) process. Two xanthate-type chain transfer agents (CTAs), *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 1) and *O*-ethyl-*S*-(1-ethoxycarbonyl) ethyldithiocarbonate (CTA 2), proved efficient for obtaining poly(PVI-Br)s and (EHVI-Br)s with relatively low polydispersities ($M_w/M_n < 1.4$). Poly(EtOEVI-Br)s with moderate molecular weight distributions ($M_w/M_n = 1.5-1.6$) were also obtained under the same conditions. Controlled character of the polymerization of PVI-Br was confirmed by the molecular weight controlled by the monomer/CTA molar ratio, a linear increase in the number-average molecular weight (M_n) with conversion, and the ability to extend the chain by a second addition of monomer. Polymerizations of the *N*-vinylimidazolium salts using the dithiocarbonate-terminated poly(*N*-isopropylacrylamide) as a macro-chain-transfer agent provided well-defined thermoresponsive ionic liquid block copolymers. Thermally induced phase separation behavior and assembled structures of the block copolymers were also studied in aqueous solution.

Introduction

Ionic liquids, which are organic salts having low melting temperature, have attracted significant research interest because of their characteristic properties including high ionic conductivity, high polarity, high density, high heat capacity, and high thermal and chemical stability.[1−5] Ionic liquids are becoming widely recognized as environmentally friendly reaction media "green solvents", replacing volatile organic solvents, which is mainly due to their nonflammability and nonvolatility.[1,2] Another advantage of using these ionic liquids is their ability to dissolve a wide range of organic and ionic compounds. Recently, much effort has been directed at the usage of ionic liquids as green solvents for various polymerization systems.[4] Another recent progress in this field involves the development of temperature-dependent self-assembly system of polybutadiene-*b*-poly(ethylene oxide) amphiphilic block copolymers in ionic liquid.[6,7] Unique and attractive properties of ionic liquids can be tuned widely by adjusting the structures of the cation (e.g., imidazolium, pyridinium, and tetraalkylammonium) and the anion (e.g., halide, tetrafluoroborate, hexafluorophosphate).

Recently, much attention has been paid to polymerized ionic liquids or polymeric ionic liquids, which are macromolecules obtained from polymerizing ionic liquid monomers.[8] Their potential applications involve polymeric electrolytes,[5,9−11] catalytic membranes,[12] ionic conductive materials,[13−15] CO_2 absorbing materials,[16−19] microwave absorbing materials,[20,21] and porous materials.[22,23] A variety of polymers having imidazolium moieties in the side chains have been reported, including poly(meth)acrylate,[14,24−26] polystyrene,[18,27] and poly(*N*-vinylimidazolium)[21,28−30] derivatives, and most of these poly(ionic liquid)s were prepared by conventional radical polymerizations. Free radical polymerizations of various *N*-vinylimidazolium derivatives were reported to proceed in the presence of conventional radical initiator, and various copolymers involving the imidazolium group were also synthesized by this method.[31,32]

Recent significant progress of controlled/living radical polymerization techniques, such as nitroxide-mediated polymerization,[33] atom transfer radical polymerization,[34,35] and reversible addition−fragmentation chain transfer (RAFT) polymerization,[36−49] has allowed for the synthesis of functional polymers with controlled molecular weights, low polydispersity, and complex architectures. Attempts to synthesize well-defined block polymers containing the imidazolium groups using controlled radical polymerizations have appeared in the literature. Waymouth et al. demonstrated the synthesis of a series of block copolymers comprising a polystyrene and an imidazolium-functionalized polystyrene by nitroxide-mediated polymerization, followed by postsynthesis modification of the chloromethyl group.[50,51] They also characterized their assembly properties of the imidazolium-functionalized block copolymers. Recently, Gnanou et al. reported the synthesis of double hydrophilic block copolymers having ionic responsive property by RAFT polymerizations of methacrylate-type ionic liquids.[52] These double hydrophilic block copolymers composed of an imidazolium-functionalized segment and a poly(methacrylic acid) segment were found to self-assemble in micelle-like structures in water by exchanging the counteranion of the ionic liquid segment. RAFT polymerization was also employed for the synthesis of block copolymers containing the imidazolium and thiazole groups, which showed characteristic magnetic properties.[53] Another example involves RAFT synthesis of block copolymers comprising of *N*-vinylimidazole,[54] which can be regarded as a precursor of *N*-vinylimidazolium salts. Atom transfer radical polymerization of methacrylate[24] and styrene[27] derivatives having the imidazolium groups were also reported.

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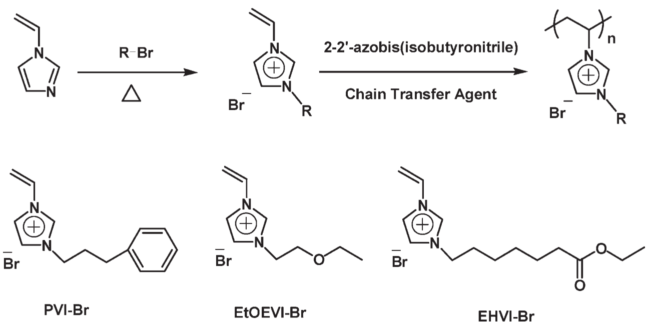
Scheme 1. Synthesis of Poly(*N*-vinylimidazolium Salt)s and Structures of *N*-Vinylimidazolium Salts



Scheme 2. Structures of Chain Transfer Agents (CTAs)


CTA 1 CTA 2

We now report the synthesis of poly(*N*-vinylimidazolium salt)s with controlled molecular weights and narrow polydispersity by RAFT polymerization of ionic *N*-vinyl monomers (Scheme 1). Three *N*-vinylimidazolium salts having different substituent groups were selected in this study in order to manipulate the properties of resulting polymeric ionic liquids. Among various controlled radical polymerizations, in this study, we selected RAFT polymerization[36−49] because of versatility with respect to monomer type including *N*-vinyl and *O*-vinyl nonconjugated monomers as well as ionic monomers. In general, controlled radical polymerization of *N*-vinyl and *O*-vinyl monomers had been difficult until recent years, since the generated radical species are highly reactive due to their nonconjugated nature and strong electron-donating pendant groups. Recent progress of 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 useful for controlling the radical polymerization of *O*-vinyl and *N*-vinyl monomers, such as vinyl acetate[55−57] and *N*-vinylpyrrolidone.[57−61] Recently, we also published a series of reports on the xanthate-mediated controlled radical polymerization of *N*-vinyl monomers, which involve *N*-vinylcarbazole,[62−64] *N*-vinylindole,[65] *N*-vinylphthalimide,[66] and *N*-vinylnaphthalimide.[67] In this study, we describe RAFT polymerization of the *N*-vinylimidazolium salts, which can be regarded as ionic liquid monomers having characteristic *N*-vinyl structure, and synthesis of well-defined block copolymers containing ionic poly(*N*-vinylimidazolium salt) segments. Two xanthate-type CTAs having different leaving groups were selected (Scheme 2) because a suitable selection of the leaving group is one of the important factors to achieve the controlled character by RAFT polymerization.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. 1-Vinylimidazole (Aldrich, 99%) and *N*,*N*-dimethylformamide (DMF, Kanto Chemical, 99.0%) were dried with CaH_2 for 2 h and distilled under vacuum. *N*-Isopropylacrylamide (NIPAAm, Tokyo Kasei Kogyo, 98%) was purified by recrystallization from *n*-hexane/$CHCl_3$ (5/1 vol %). 3-Bromopropylbenzene (Kanto Chemical, 97%), ethyl 7-bromoheptanoate (Aldrich, 97%), and 2-bromodiethyl ether (Tokyo Kasei Kogyo, 95%) were used as received. Other materials were used without further purification.

Synthesis of Chain Transfer Agents (CTAs). *O*-Ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 1)[62,68,69] and *O*-ethyl-*S*-(1-ethoxycarbonyl) ethyldithiocarbonate (CTA 2)[66,70] (Scheme 2) were synthesized by the reaction of potassium ethyl xanthogenate with corresponding bromide (1-bromoethylbenzene for CTA 1 and ethyl 2-bromopropanoate for CTA 2) in accordance with the 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. ^{1}H NMR spectra of CTAs are shown in Figure S1 (see Supporting Information).

Synthesis of *N*-Vinylimidazolium Salts. Three *N*-vinylimidazolium salts having different substituent groups, 1-(3-phenylpropyl)-3-vinylimidazolium bromide (PVI-Br), 1-(6-ethoxycarbonylhexyl)-3-vinylimidazolium bromide (EHVI-Br), and 1-(2-ethoxyethyl)-3-vinylimidazolium bromide (EtOEVI-Br), were synthesized by the reaction of 1-vinylimidazole with corresponding alkyl bromides according to a previously reported method with slight modifications (Scheme 1).[29] In a typical experiment, 13.6 mL of 3-bromopropylbenzene (18.3 g, 0.0918 mol) was added dropwise to 4.82 mL of 1-vinylimidazole (5.00 g, 0.0531 mol) under stirring. The mixture was stirred at 40 °C for 16 h. After the resulting yellow viscous liquid was washed several times with ethyl acetate by decantation, the product was dried under vacuum overnight at room temperature to afford PVI-Br as a pale yellow viscous liquid (12.1 g, 83%). ^{1}H NMR ($CDCl_3$): δ 10.5 (s, 1H, $-N-CH-N-$), 7.9 (s, 1H, $-N-CHCH-N-$), 7.6 (s, 1H, $-N-CHCH-N-$), 7.4 (dd, 1H, $CH_2{=}CH-N-$), 7.3−7.2 (m, 5H, $-C_6H_5$), 6.0 (dd 1H, $CH_2{=}CH-N-$), 5.4 (dd, 1H, $CH_2{=}CH-N-$), 4.4 (t, 2H, $-N-CH_2-CH_2-$), 2.9−2.7 (m, 2H, $-CH_2-CH_2-CH_2-$), 2.3 ppm (m, 2H, $-CH_2-CH_2-C_6H_5$). ^{13}C NMR ($CDCl_3$): δ 139.6 ($-CH_2-C$ in C_6H_5), 136.2 ($-N-CH-N-$), 128.4 ($-C_6H_5$), 126.4 ($CH_2{=}CH-$), 122.7 ($-N-CHCH-N-$), 118.2 ($-N-CHCH-N-$), 109.9 ($CH_2{=}CH-$), 49.7 ($-N-CH_2-$), 31.6 ($-CH_2-CH_2-C_6H_5$), and 30.8 ppm ($-CH_2-CH_2-C_6H_5$).

The same procedure was employed for the synthesis of EtOEVI-Br. By the reaction of 1-vinylimidazole with 2-bromodiethyl ether under the same reaction conditions, followed by the decantation with ethyl acetate, EtOEVI-Br was obtained as a yellow viscous liquid (46%). ^{1}H NMR ($CDCl_3$): δ 10.2 (s, 1H, $-N-CH-N-$), 7.9 (s, 1H, $-N-CHCH-N-$), 7.5 (s, 1H, $-N-CH-CH-N-$), 7.3 (dd, 1H, $CH_2{=}CH-N-$), 5.8 (dd, 1H, $CH_2{=}CH-N-$), 5.2 (dd, 1H, $CH_2{=}CH-N-$), 4.4 (t, 2H, $-N-CH_2-CH_2-$), 3.6 (t, 2H, $-CH_2-CH_2-O-$), 3.3 (m, 2H, $-O-CH_2-CH_3$), 0.9 ppm (t, 3H, $-O-CH_2-CH_3$). ^{13}C NMR ($CDCl_3$): δ 136.2 ($-N-CH-N-$), 126.4 ($CH_2{=}CH-$), 123.9 ($-N-CHCH-N-$), 119.3 ($-N-CHCH-N-$), 109.9 ($CH_2{=}CH-$), 68.2 ($-O-CH_2-$), 66.7 ($-O-CH_2-$), 49.7 ($-N-CH_2-$), and 14.2 ppm ($-CH_3$).

Similarly, EHVI-Br was obtained by the reaction of 1-vinylimidazole with ethyl 7-bromoheptanoate. After the crude product was washed several times with ethyl acetate by decantation, it was purified by reprecipitation from a small amount of MeOH into ethyl acetate. EHVI-Br was obtained as a white solid (48%, mp = 81 °C). ^{1}H NMR ($CDCl_3$): δ 11.0 (s, 1H, $-N-CH-N-$), 7.8 (s, 1H, $-N-CHCH-N-$), 7.5 (s, 1H, $-N-CHCH-N-$), 7.4 (dd, 1H, $CH_2{=}CH-N-$), 5.9 (dd, 1H, $CH_2{=}CH-N-$), 5.4 (dd, 1H, $CH_2{=}CH-N-$), 4.4 (t, 2H, $-N-CH_2-CH_2-$), 4.0 (m, 2H, $-COO-CH_2-CH_3$), 2.3 (t, 2H, $-CH_2-COO-$), 1.9 (m, 2H, $-N-CH_2-CH_2-$), 1.5 (m, 2H, $-CH_2-CH_2-COO-$), 1.3 (m, 4H, $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$), 1.2 ppm (t, 3H, $-COO-CH_2-CH_3$). ^{13}C NMR ($CDCl_3$): δ 173.5 ($C{=}O$), 136.2 ($-N-CH-N-$), 126.4 ($CH_2{=}CH-$), 123.9 ($-N-CHCH-N-$), 119.3 ($-N-CHCH-N-$), 109.9 ($CH_2{=}CH-$), 60.4 ($COO-CH_2-CH_3$), 50.1 ($-N-CH_2-$), 33.9 ($-CH_2-$), 29.9 ($-CH_2-$), 28.2 ($-CH_2-$), 25.8 ($-CH_2-$), 24.4 ($-CH_2-$), and 14.2 ppm ($-CH_3$). ^{1}H and ^{13}C NMR spectra and solubilities of these monomers are shown in Figures S2−S4 and Tables S1−S3, respectively (see Supporting Information).

General Polymerization Procedure. All polymerizations were carried out with AIBN as the initiator in a degassed sealed tube. A representative example is as follows: PVI-Br (0.267 g, 0.91 mmol), CTA 1 (4.1 mg, 0.018 mmol), AIBN (1.5 mg, 0.009 mmol), and DMF (1.0 mL) were placed in a dry glass ampule equipped with a magnetic stirring 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 20 h. 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 CD_3OD at room temperature, and the integration of the monomer $\text{C{=}C}{-}H$ resonance at around 5.9 ppm was compared with the sum of $\text{N}{-}\text{C}H{-}\text{N}$ peak intensity of the imidazolium ring in the polymer and the monomer at around 9.4−9.9 ppm. Conversion determined by this method was 72%. The crude polymer was purified by reprecipitation into a large excess of acetone, and the resulting product was dried under vacuum at room temperature: yield 0.163 g, 61%. ^{1}H NMR (CD_3OD): δ 9.9−9.4 (1H, $-\text{N}{-}\text{C}H{-}\text{N}{-}$), 8.2−7.7 (1H, $-\text{N}{-}\text{CHC}H{-}\text{N}{-}$), 7.7−7.3 (1H, $-\text{N}{-}\text{C}H\text{CH}{-}\text{N}{-}$), 7.2 (5H, $-\text{C}_6H_5$), 5.0−4.7 (1H, CH in the main chain), 4.4−3.8 (2H, $-\text{N}{-}\text{C}H_2{-}\text{CH}_2{-}$), 3.0−2.7 ($-\text{CH}_2{-}\text{C}H_2{-}\text{CH}_2{-}$), 2.7−2.4 (2H, C$H_2$ in the main chain), 2.4−2.0 ppm (2H, $-\text{CH}_2{-}\text{C}H_2{-}\text{C}_6\text{H}_5$). The ^{1}H NMR spectrum of poly(PVI-Br) is shown in Figure S5 (see Supporting Information). The resulting poly(PVI-Br) was soluble in methanol, DMSO, DMF, and chloroform and insoluble in water, ethyl acetate, acetone, THF, diethyl ether, and hexane.

In the case of the polymerization of EtOEVI-Br, the crude polymer was purified by reprecipitation into a large excess of acetone/diethyl ether (8/2 vol %). In contrast, the purification of the crude polymer obtained by the polymerization of EHVI-Br was conducted by reprecipitation into a large excess of acetone/diethyl ether (1/1 vol %). ^{1}H NMR spectra of these polymers are shown in Figure S5 (see Supporting Information). Poly(EtOEVI-Br) and poly(EHVI-Br) were also soluble in methanol, DMSO, DMF, and chloroform. Additionally, poly(EtOEVI-Br) was soluble in water, and poly(EHVI-Br) was soluble in acetone. The solubilities of these polymers in various solvents are summarized in Tables S1−S3 (see Supporting Information).

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

$$M_\text{n}(\text{theor}) = \frac{[\text{monomer}]_0}{[\text{CTA}]_0 + 2f[\text{I}]_0(1 - \text{e}^{-k_\text{d}t})} \times M_\text{monomer} \times \text{conv} + M_\text{CTA} \tag{1}$$

in which M_CTA and M_monomer are the molecular weights of CTA and the monomer, and $[\text{monomer}]_0$ and $[\text{CTA}]_0$ are the initial concentrations of the monomer and CTA, respectively. The right-hand side of the denominator accounts for the radicals derived from the initiator with an initial concentration $[\text{I}]_0$ at time t and a decomposition rate, k_d. The initiator efficiency is represented by f. Note that eq 1 is only effective for the disproportional termination. In an ideal RAFT process, the polymer directly derived from the initiators is considered to be minimal, and thus the second term in the denominator becomes negligible and eq 1 can be simplified to eq 2:[40,41,43]

$$M_\text{n}(\text{theor}) = \frac{[\text{monomer}]_0}{[\text{CTA}]_0} \times M_\text{monomer} \times \text{conv} + M_\text{CTA} \tag{2}$$

For the kinetic study, typically a mixed solution of PVI-Br (2.66 g, 9.10 mmol), CTA 1 (20.6 mg, 0.0910 mmol), AIBN (7.5 mg, 0.0455 mmol), and DMF (10 mL) was divided into five glass ampules, and then each solution was degassed by three freeze−evacuate−thaw cycles. After the ampule was sealed by flame under vacuum, it was stirred at 60 °C for the desired time. The reaction was stopped by rapid cooling with liquid nitrogen, and the monomer conversion was determined by the ^{1}H NMR spectrum of the polymerization mixture.

Synthesis of Block Copolymers. A representative example of the synthesis of the block copolymer composed of NIPAAm and PVI-Br is as follows: NIPAAm (1.03 g, 9.10 mmol), CTA 1 (20.5 mg, 0.091 mmol), AIBN (1.5 mg, 0.009 mmol), and 1,4-dioxane (3.6 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 80 °C for 6 h. After the product was purified by precipitation into diethyl ether, the product was dried under vacuum at 40 °C to afford poly(NIPAAm) as a white solid (0.896 g, 87%, M_n = 8100 g/mol, M_w/M_n = 1.34, conversion = 88%), which was employed as a macro-CTA.

The dithiocarbonate-terminated poly(NIPAAm) (0.111 g, 0.0182 mmol), AIBN (1.5 mg, 0.009 mmol), PVI-Br (0.267 g, 0.91 mmol), and DMF (2.0 mL) were placed in a dry ampule. After the solution was degassed by three freeze−evacuate−thaw cycles, the polymerization was conducted at 60 °C for 20 h (conversion determined by ^{1}H NMR spectroscopy = 68%). The reaction mixture was purified by reprecipitation into acetone and isolated by filtration to give a double-hydrophilic block copolymer, poly(NIPAAm)-*b*-poly(PVI-Br), as a pale yellow viscous material (0.231 g, 61%). The block copolymer was soluble in methanol, DMSO, DMF, and chloroform and insoluble in ethyl acetate, dioxane, diethyl ether, and hexane.

The copolymer composition was determined using ^{1}H NMR spectroscopy by a comparison of peaks associated with the two comonomers. The peak at 9.1−10.0 ppm is attributed the $\text{N}{-}\text{C}H{-}\text{N}$ proton of the imidazolium ring in PVI-Br unit, whereas the peak at 0.8−1.0 ppm corresponds to the methyl protons of the NIPAAm units. Thus, the comonomer composition can be calculated using the eq 3 as follows:

$$\frac{1(x)}{6(1-x)} = \frac{\text{integral at } 9.1 - 10.0 \text{ ppm}}{\text{integral at } 0.8 - 1.0 \text{ ppm}} \tag{3}$$

Here x is the fraction of the PVI-Br and $1 - x$ is the fraction of NIPAAm 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. The 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 RALLS; wavelength = 670 nm). The column set was as follows: two consecutive columns [Tosoh TSK-GELs (exclusion limited molecular weight): G5000PW$_\text{XL}$-CP (1×10^6), G3000PW$_\text{XL}$-CP (9×10^4), 30 cm each] and a guard column [TSK-guardcolumn PW$_\text{XL}$-CP, 4.0 cm]. The system was operated at a flow rate of 1.0 mL/min using acetonitrile/water (50/50 vol %) containing 0.05 M NaNO_3 as an eluent. Poly(ethylene oxide) standards were employed for calibration.

The phase separation temperatures of the aqueous solutions of the block copolymers (2.0 mg/mL) were measured by monitoring the transmittance of a 500 nm light beam through a quartz sample cell. The transmittance was recorded on a JASCO V-630BIO UV−vis spectrophotometer equipped with temperature controller system (JASCO EHC-716 and EHC-717). The temperature was increased at a rate of 1.0 °C/min in heating scans between 25 and 60 °C.

Dynamic light scattering (DLS) was performed at 25 °C by an Otsuka Electronics DLS-7000 spectrometer with a He−Ne laser (λ_0 = 632.8 nm) at the scattering angle of 90°. Prior to the light scattering measurement, the polymer solution was filtered using Millipore Teflon filters with a pore size of 0.2 μm into a dust-free cylindrical cuvette.

Results and Discussion

RAFT Polymerization of *N*-Vinylimidazolium Salts. In this study, we focused on *N*-vinylimidazolium salts having

Table 1. Polymerization of *N*-Vinylimidazolium Salts Using 2,2′-Azobis(isobutyronitrile) (AIBN) in *N*,*N*′-Dimethylformamide (DMF) at 60 °C for 20 h[a]

				M_n (g/mol)		
run	monomer[b]	CTA[c]	conv[d] (%)	theory[e]	SEC[f]	M_w/M_n[f] (SEC)
1[g]	PVI-Br		> 99		51 900	1.89
2		CTA 1	72	10 600	25 300	1.32
3		CTA 2	77	11 500	25 600	1.39
4[g,h]	EtOEVI-Br		55		42 000	2.23
5		CTA 1	62	7 900	22 200	1.53
6		CAT 2	65	8 200	23 600	1.56
7[g]	EHVI-Br		94		195 100	1.87
8		CTA 1	46	8 500	11 000	1.26
9		CTA 2	50	9 200	12 100	1.27

[a] [M]/[CTA]/[AIBN] = 100/2/1, monomer concentration = 0.9 M. [b] PVI-Br = 1-(3-phenylpropyl)-3-vinylimidazolium bromide, EtOEVI-Br = 1-(2-ethoxyethyl)-3-vinylimidazolium bromide, and EHVI-Br = 1-(6-ethoxycarbonylhexyl)-3-vinylimidazolium bromide. [c] CTA 1 = *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate and CTA 2 = *O*-ethyl-*S*-(ethoxycarbonyl) ethyldithiocarbonate. [d] Calculated by ^{1}H NMR in $CDCl_3$. [e] $M_{n(theory)}$ = MW of monomer × [M]/[CTA] × conv + MW of CTA. [f] Measured by SEC using poly(ethylene oxide) standards in H_2O/acetonitrile (50/50 vol % containing 0.05 M $NaNO_3$). [g] [M]/[AIBN] = 100/1. [h] Polymerization for 2 h.

different substituent groups, 1-(3-phenylpropyl)-3-vinylimidazolium bromide (PVI-Br), 1-(6-ethoxycarbonylhexyl)-3-vinylimidazolium bromide (EHVI-Br), and 1-(2-ethoxyethyl)-3-vinylimidazolium bromide (EtOEVI-Br), as shown in Scheme 1. Different from (meth)acrylate and styrene-type ionic liquid monomers, the direct linkage of the imidazolium group to the polymer main chain is an important feature of these monomers because it may affect not only the polymerization behavior but also various properties of the resulting poly(ionic liquid)s. These monomers were synthesized by the reaction of 1-vinylimidazole with corresponding alkyl bromides according to a previously reported method with slight modifications.[29] Since there are many alkylating reagents available, the properties of the corresponding polymeric ionic liquids can be varied as a function of the lateral chains. Both PVI-Br and EtOEVI-Br were liquid at room temperature, which can be regarded as ionic liquid monomers. In contrast, EHVI-Br was obtained as a solid. All monomers were soluble in water, methanol, chloroform, DMSO, and DMF and insoluble in ethyl acetate, THF, dioxane, diethyl ether, and hexane.

Conventional radical polymerization of the *N*-vinylimidazolium salts was initially conducted with AIBN at $[M]_0/[AIBN]_0$ = 100 in DMF at 60 °C for 20 h in order to find conditions for obtaining polymeric products having relatively high molecular weights with sufficient yields. The results are summarized in Table 1. The polymerization of PVI-Br proceeded homogeneously under the condition, and the polymer having relatively high molecular weight (M_n = 51 900 g/mol, M_w/M_n = 1.89, conversion > 99%) was obtained as a white solid after the precipitation into acetone. In contrast, the polymerization of EtOEVI-Br under the same conditions afforded insoluble product after 20 h, whereas the soluble polymer having reasonable molecular weights (M_n = 42 000 g/mol, M_w/M_n = 2.23, conversion = 55%) was obtained by the polymerization for 2 h. In the case of the polymerization of EHVI-Br, higher molecular weight product was obtained (M_n = 195 100 g/mol, M_w/M_n = 1.87, conversion = 94%) after 20 h.

The polymerization of the *N*-vinylimidazolium salts was conducted with two xanthate-type CTAs and AIBN as an initiator 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) in DMF at 60 °C. The results are summarized in Table 1 and Figure 1. The RAFT polymerization of PVI-Br afforded the polymers having relatively low polydispersities (M_w/M_n = 1.32−1.39) with reasonable conversions (72−77%, as determined by ^{1}H NMR spectroscopy), regardless of the nature of CTA. For the determination of molecular weights and molecular weight distributions of the poly(*N*-vinylimidazolium salt)s, we employed special GPC columns, which were applicable for cationic polymers, and the GPC measurement was conducted in acetonitrile/water (50/50 vol %) containing 0.05 M $NaNO_3$ as an eluent. As can be seen in Figure 1a, the GPC traces of poly(PVI-Br)s prepared with CTAs are unimodal with no evidence of high and low molecular weight species. In both cases, the molecular weights of the poly(PVI-Br)s, measured by the GPC, were apparently higher than the theoretical values calculated from the monomer/CTA molar ratio and conversion of the monomer. These discrepancies are believed to result from the difference in hydrodynamic volume between poly(PVI-Br)s and the linear poly(ethylene oxide) standards used for GPC calibration. The molecular weights obtained by the GPC using poly(ethylene oxide) calibration are just the apparent ones due to the lack of suitable standards. Nevertheless, the significant difference in the molecular weights of the polymers obtained in the

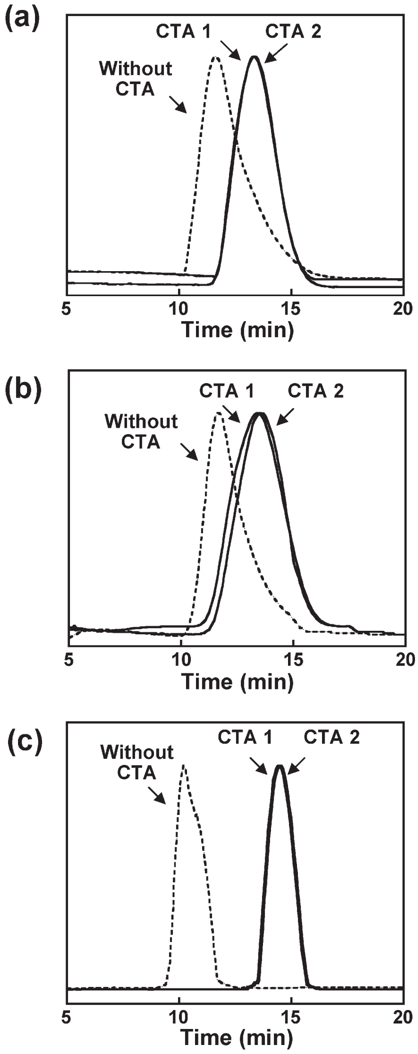


Figure 1. SEC traces of (a) poly(PVI-Br)s, (b) poly(EtOEVI-Br)s, and (c) poly(EHVI-Br)s obtained with and without chain transfer agent (CTA 1 and CTA 2). See Table 1 for detailed polymerization conditions.

Scheme 3. Proposed Mechanism of Xanthate-Mediated Controlled Radical Polymerization of *N*-Vinylimidazolium Salt

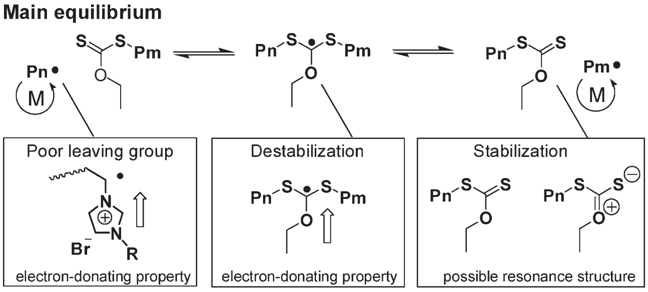


Table 2. RAFT Polymerization of 1-(3-Phenylpropyl)-3-vinylimidazolium Bromide (PVI-Br) Using 2,2′-Azobis(isobutyronitrile) (AIBN) in *N*,*N*′-Dimethylformamide (DMF) at 60 °C for 20 h[a]

				M_n (g/mol)			
run	CTA[b]	[M]/[CTA]	conv[c] (%)	theory[d]	NMR[c]	SEC[e]	M_w/M_n[e] (SEC)
1	CTA 1	10	73	2 400	4 100	10 200	1.22
2		50	72	10 600	8 800	25 300	1.32
3		100	78	23 200	24 900	35 600	1.37
4		150	74	32 800	36 200	55 900	1.19
5	CTA 2	10	73	2 400	3 500	11 100	1.28
6		50	77	11 500	7 800	25 600	1.39

[a] [CTA]/[AIBN] = 2, monomer concentration = 0.9 M. [b] CTA 1 = *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate and CTA 2 = *O*-ethyl-*S*-(ethoxycarbonyl) ethyldithiocarbonate. [c] Calculated by ^{1}H NMR in $CDCl_3$. [d] $M_{n(theory)}$ = MW of PVI-Br × [M]/[CTA] × conv + MW of CTA. [e] Measured by SEC using poly(ethylene oxide) standards in H_2O/acetonitrile (50/50 vol % containing 0.05 M $NaNO_3$).

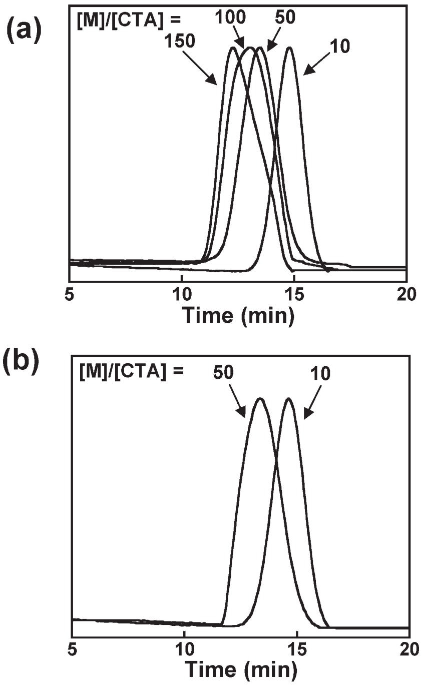


Figure 2. SEC traces of poly(PVI-Br)s obtained with (a) CTA 1 and (b) CTA 2 at different [M]/[CTA] ratios. See Table 2 for detailed polymerization conditions.

presence and absence of CTA may support the effective chain transfer under the reaction conditions.

RAFT polymerization of EHVI-Br with both CTAs afforded poly(EHVI-Br)s having narrow molecular weight distributions (M_w/M_n = 1.26−1.27, M_n = 11 000−12 100 g/mol) with moderate monomer conversions (46−50%). These results suggest that the xanthate-type CTAs act as mediating agents to produce poly(*N*-vinylimidazolium salt)s having relatively low polydispersities, whereas no significant difference is detected between CTA 1 and CTA 2 on the polydispersity, molecular weight, and polymerization rate. The molecular weight distributions (M_w/M_n = 1.53−1.56) of poly(EtOEVI-Br)s prepared by RAFT polymerization were slightly broader than those of poly(PVI-Br) and poly(EHVI-Br). RAFT polymerization of EtOEVI-Br at higher [CTA]/[AIBN] ratios led to the drastic decrease in the conversion (for example, polymer yields were less than 10% at [CTA 1] /[AIBN] = 5 and 10 under the same conditions). Nevertheless, these results support our strategy that MADIX polymerization utilizing *O*-alkyl xanthates as CTAs is a very efficient method to control the polymerization of highly reactive propagating radicals like those deriving from vinyl acetate or *N*-vinyl monomers, when the leaving group is properly chosen.[55−67] 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 to afford controlled radical polymerization of *N*-vinylimidazolium salt using the xanthate-type CTA. In other words, these results suggest that the reactivity of propagating *N*-vinylimidazolium salt radical is comparable to that of typical *N*-vinyl monomers, even if the vinyl group is directly connected to the imidazolium ring in the ionic liquid monomers used in this study.

With a view to preparing poly(*N*-vinylimidazolium salt)s over a wide range of molar mass, different degrees of polymerization were targeted. For this purpose, the polymerization of PVI-Br was conducted at different $[M]_0/[CTA\ 1]_0$ ratios between 10 and 150, while the AIBN/CTA 1 molar ratio was held constant at 1/2. When the polymerizations were conducted in DMF at 60 °C for 20 h, the conversions were nearly 70−80% (determined by ^{1}H NMR spectroscopy), as shown in Table 2. The number-average molecular weights of the poly(PVI-Br)s increase with the [M]/[CTA] ratio, and the molecular weight distributions remain narrow (M_w/M_n = 1.19−1.37), indicating the feasibility of controlling the molecular weights. In all cases, the SEC traces are unimodal with no evidence of high molecular weight species (Figure 2). When the polymerizations were conducted with CTA 2, the same tendency was observed in terms of the molecular weight controlled by the monomer/CTA molar ratio with maintaining low polydispersity. These results suggest that poly(PVI-Br)s having predetermined molecular weights and relatively low polydispersities can be easily obtained by direct RAFT polymerization of *N*-vinylimidazolium salt.

The NMR technique was used to determine the chain-end structure and absolute molecular weights of poly(PVI-Br)s. The CTA-derived initiator may produce the polymer with CTA fragments at the polymer chain ends (α-chain end with the 1-phenylethyl group and ω-chain end with the dithiocarbonate group in the case of CTA 1). The ^{1}H NMR spectra of the poly(PVI-Br)s obtained at different $[PVI\text{-}Br]_0/[CTA\ 1]_0$ ratios is presented in Figure 3. The characteristic peaks at 9.9−9.4 ppm (−N−C*H*−N−), 8.2−7.2 ppm (−N−C*H*C*H*−N− and $-C_6H_5$), and 4.4−3.8 ppm ($-N-CH_2-CH_2-$) are clearly seen, which are attributed to poly(PVI-Br) main

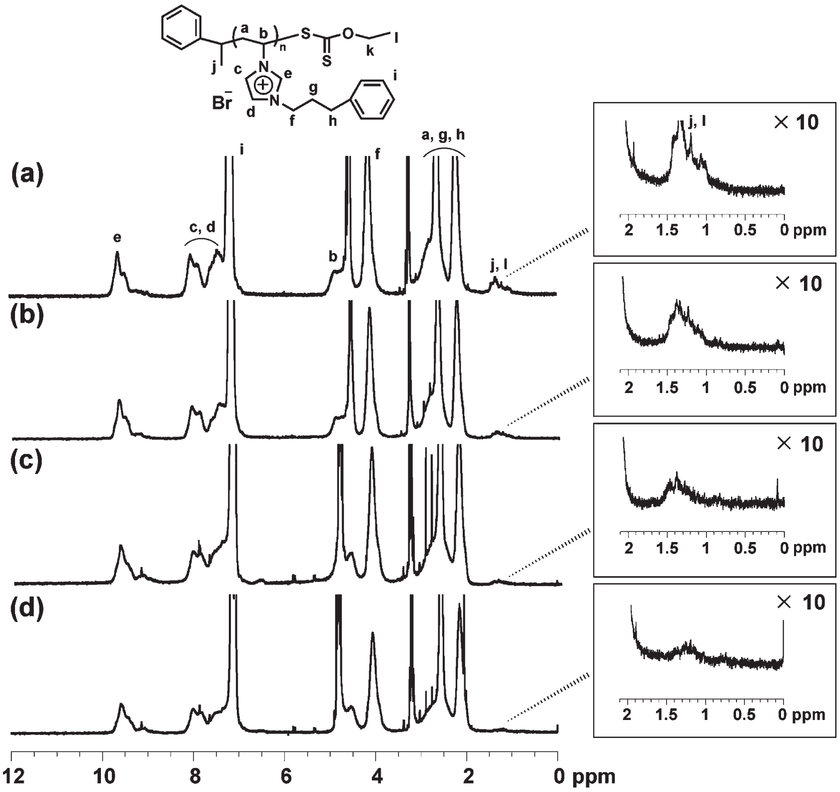


Figure 3. ^{1}H NMR spectra (CD_3OD) of poly(PVI-Br)s obtained at [PVI-Br]/[CTA 1] = (a) 10, (b) 50, (c) 100, and (d) 150.

chain. In addition to these peaks, methyl protons are clearly visible at 0.5−1.5 ppm, which correspond to the ethoxy and 1-phenylethyl 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 general mechanism of the RAFT process. The chain-end structures were also detected in the polymer obtained with CTA 2 (Figure S6, see Supporting Information). 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(PVI-Br) prepared with CTA 1 can be calculated by comparison of the area of the peak at 9.9−9.4 ppm corresponding to the methine proton in the imidazolium ring (peak "e" in Figure 3) in PVI-Br repeating units to the peak at 0.5−1.5 ppm (peaks "j and l") corresponding to six protons of two different types of methyl protons of end groups. As shown in Table 2, the molecular weights determined by NMR are comparable to the theoretical values calculated using the eq 2, which are apparently lower than those obtained from SEC using poly(ethylene oxide) standards.

Polymerization Kinetics. The kinetics of this RAFT polymerization was investigated. Figure 4a shows the variation in $\ln([M]_0/[M]_t)$ versus polymerization time for the polymerization of PVI-Br in DMF at 60 °C with AIBN in the presence of CTA 1. When the reaction was conducted at $[\text{PVI-Br}]_0/[\text{CTA 1}]_0:[\text{AIBN}]_0 = 200/2/1$, an almost full conversion was reached after 36 h. An almost linear first-order kinetic plot is seen until 50% conversion. Nevertheless, a linear increase in the number-average molecular weight determined by ^{1}H NMR spectroscopy with conversion is observed, indicating a constant number of propagating chains throughout the polymerization (Figure 4b). The SEC traces (refractive index) of poly(PVI-Br)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 ($M_w/M_n = 1.26-1.29$) is seen, as normally evidenced for a controlled/living 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 combination of the growing polymer chains during a longer reaction time.

As shown in Figure 4a, an induction period of less than 5 h is seen in the pseudo-first-order kinetic plot at $[\text{PVI-Br}]_0/[\text{CTA 1}]_0 = 100/1$. A similar induction period was also observed at lower monomer to CTA molar ratio ($[\text{PVI-Br}]_0/[\text{CTA 1}]_0 = 50/1$; see Figure S7, Supporting Information). In both cases, the induction periods roughly estimated simply by extrapolating the linear part of each curve to the time axis are about 2 h. An induction period is often observed during the RAFT/MADIX polymerization of *N*-vinyl monomers.[59,62,65,66] No significant influence of the monomer to CTA molar ratio was detected on the polymerization rate, namely retardation. There is an ongoing debate on the mechanism that causes the inhibition and retardation.[44] A drastic increase in the rate, $\ln([M]_0/[M]_t)$, at the last stage of the polymerization was detected in the pseudo-first-order kinetic plot at $[\text{PVI-Br}]_0/[\text{CTA 1}]_0/[\text{AIBN}]_0 = 200/2/1$ (Figure 4a). This may be due to autoacceleration (gel effect) of high molecular weight product at higher monomer conversions because an almost linear first-order kinetic plot was observed at lower monomer to CTA molar ratio (see Figure S7, Supporting Information). Another possible explanation is that nonlinear first-order kinetic plot is related to unexpected side reactions, which were observed in xanthate-mediated polymerization of another *N*-vinyl monomer.[61]

Chain Extension. An important criterion of 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(PVI-Br) ($M_{n,SEC}$ = 10 200 g/mol, $M_{n,NMR}$ = 4100 g/mol, M_w/M_n = 1.18) prepared by the

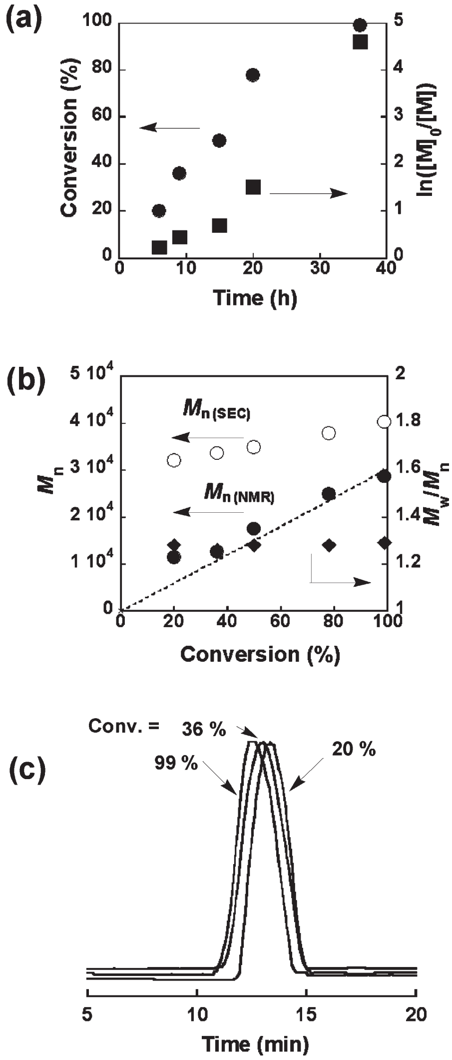


Figure 4. (a) Time−conversion (circles) and first-order kinetic (squares) plots for the polymerization of 1-(3-phenylpropyl)-3-vinylimidazolium bromide (PVI-Br) with 2,2′-azobis(isobutyronitrile) (AIBN) in the presence of *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 1, see Scheme 2) in DMF at 60 °C. [PVI-Br]$_0$/[CTA 1]$_0$/[AIBN]$_0$ = 200/2/1. (b) Number-average molecular weights determined by SEC (open circles) and ^{1}H NMR (closed circles) and polydispersity (squares) as a function of conversion. (c) Evolution of SEC traces of poly(PVI-Br)s with conversion.

polymerization using CTA 1 was employed as a macro-CTA for chain extension experiment. After 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 [PVI-Br]$_0$/[macro-CTA]$_0$/[AIBN]$_0$ = 100/2/1, the conversion was 77% after 20 h, and the polymer was recovered by precipitation in acetone. The relatively high efficiency (percentage of macro-CTA converted to extended polymer) was confirmed by the clear shift in the SEC traces for the macro-CTA and the corresponding polymer (Figure 5). The extended polymer exhibited a symmetrical SEC peak with a relatively low polydispersity (M_w/M_n = 1.27). These results suggest that most of the chain ends of the poly(PVI-Br) are functionalized with the dithiocarbonate end groups, which can be used as a macro-CTA for further chain extension reactions.

Synthesis of Block Copolymers. We attempted the synthesis of novel block copolymers comprising poly(*N*-vinylimidazolium salt) as an ionic segment and poly(NIPAAm) as a thermoresponsive segment. In this case, the xanthate-terminated poly(NIPAAm) prepared by RAFT polymerization with CTA 1 was employed as a macro-CTA for the polymerization of the *N*-vinylimidazolium salts (Scheme 4). For the synthesis of well-defined block copolymers by the RAFT process, the order of blocking is crucial. In this case, the first xanthate-terminated poly(NIPAAm) should have a high transfer constant in the subsequent polymerization of the second monomer, *N*-vinylimidazolium salts, to give the second block.[71−74] Since the propagating radical of the conjugated NIPAAm should be more stable than that of the nonconjugated *N*-vinyl monomers, the leaving ability of the propagating poly(NIPAAm) radical is greater than, or at least comparable to, that of the second poly(*N*-vinylimidazolium salt)s radical under the reaction conditions.

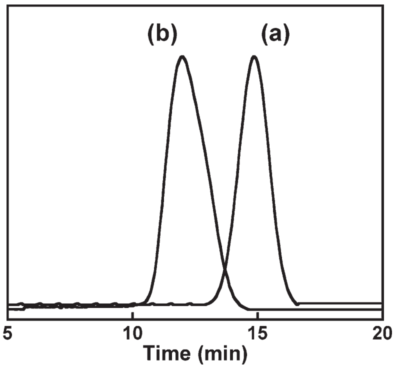


Figure 5. SEC traces of (a) the parent poly(PVI-Br) macro-CTA ($M_{n,SEC}$ = 10 200 g/mol, $M_{n,NMR}$ = 4100 g/mol, M_w/M_n = 1.18) obtained in DMF at 60 °C for 20 h and (b) the chain extended polymer (M_n = 68 300 g/mol, M_w/M_n = 1.27) obtained after the polymerization of PVI-Br in DMF at 60 °C at the ratio [PVI-Br]$_0$/[macro-CTA]$_0$/[AIBN]$_0$ = 100/2/1 for 20 h.

The polymerization of PVI-Br was initially conducted in the presence of the xanthate-terminated poly(NIPAAm) in DMF at 60 °C for 20 h. The results are summarized in Table 3. The initial CTA-to-initiator ratio ([macro-CTA]$_0$/[AIBN]$_0$) was held constant at 2/1, while the monomer to CTA ratio ([PVI-Br]$_0$/[macro-CTA]$_0$) was varied in order to control the comonomer content and the molecular weight. When the polymerization of PVI-Br was performed at 60 °C at the ratios [PVI-Br]$_0$/[macro-CTA]$_0$ = 20−250, the conversions determined by ^{1}H NMR spectroscopy were 70−50%, and the polymers were recovered by precipitations in acetone. Figure 6 shows the SEC traces of the parent poly(NIPAAm) and resulting block copolymers. A shift in the SEC trace toward higher molecular ranges is seen with increasing the [PVI-Br]/[macro-CTA] ratio. In the cases of the polymerization at high monomer to macro-CTA ratios ([PVI-Br]/[macro-CTA] ratio = 100 and 200), the block copolymers show symmetrical SEC traces with relatively low polydispersity (M_w/M_n = 1.32−1.36). A small shoulder peak is detected at high molecular weight region in the block copolymers obtained at low monomer to macro-CTA ratios ([PVI-Br]/[macro-CTA] = 20 and 50), which may be due to the unfavorable coupling reactions. Another possible explanation may be due to the difficulty of SEC measurement of the double-hydrophilic block copolymers having different contents of the ionic segment in the mixed solvent. Nevertheless, the polydispersity remain relatively low (M_w/M_n < 1.5) in all cases, and there is no significant homopolymer impurity in the block copolymers. These results suggest that the polymerization of the *N*-vinylimidazolium salt mediated by the dithiocarbonate-functionalized poly(NIPAAm) shows a reasonable control under the conditions used in this

Scheme 4. RAFT Polymerization of *N*-Vinylimidazolium Salts Using Poly(NIPAAm) as Macro-CTA

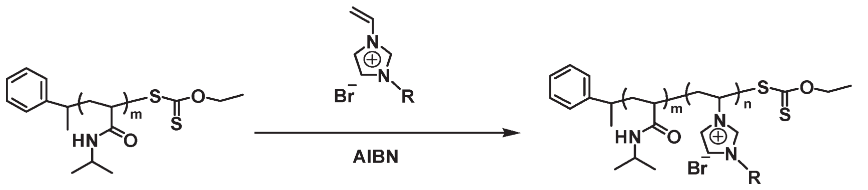


Table 3. RAFT Polymerization of 1-(3-Phenylpropyl)-3-vinylimidazolium Bromide (PVI-Br) Using Poly(NIPAAm) as a Macro-CTA at Different [M]/[Macro-CTA] Ratios in *N*,*N*′-Dimethylformamide (DMF) at 60 °C for 20 h[a]

			M_n (g/mol)				
run	[M]/[macro-CTA]	conv[b] (%)	theory[c]	NMR[b]	SEC[d]	M_w/M_n[d] (SEC)	composition[b] NIPAAm: M (theory[e])
1	20	70	12 200	14 000	18 400	1.46	55:45 (48:52)
2	50	68	18 200	17 600	27 000	1.44	46:54 (40:60)
3	100	65	27 200	23 100	56 600	1.36	37:63 (39:61)
4	250	54	44 800	27 000	80 100	1.32	30:70 (34:66)

[a] [macro-CTA]/[AIBN] = 2, monomer concentration = 0.45 M. Poly(NIPAAm): M_n = 8100 g/mol, M_w/M_n = 1.34. [b] Calculated by ^{1}H NMR in CD_3OD. [c] $M_{n(theory)}$ = MW of PVI-Br × [M]/[macro-CTA] × conv + M_n of macro-CTA . [d] Measured by SEC using poly(ethylene oxide) standards in H_2O/acetonitrile (50/50 vol % containing 0.05 M $NaNO_3$). [e] Calculated from monomer conversion, M_n value of the macro-CTA, and comonomer composition in the feed.

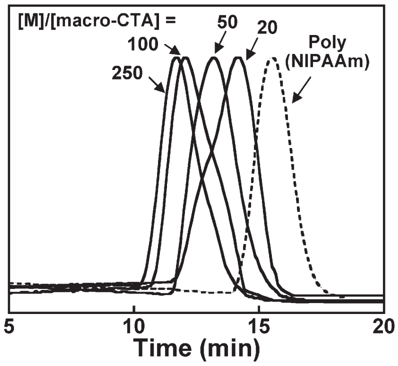


Figure 6. Evolution of SEC traces of poly(NIPAAm)-*b*-poly(PVI-Br)s obtained by polymerization of PVI-Br at different [PVI-Br]/[macro-CTA] ratios. See Table 3 for detailed polymerization conditions.

study, resulting in the formation of the well-defined block copolymers.

In all cases, the molecular weights of the block copolymers determined by SEC using poly(ethylene oxide) standards are apparently higher than the theoretical values calculated from the monomer conversion, molecular weight of the monomer unit (PVI-Br), M_n value of the macro-CTA, and the monomer composition in the feed. The ^{1}H NMR spectrum of the block copolymer, poly(NIPAAm)-*b*-poly(PVI-Br), is shown in Figure 7a. The peaks corresponding to poly(NIPAAm) and poly(PVI-Br) are clearly observed in the spectrum measured in CD_3OD. Integration of the appropriate peaks gave compositions of NIPAAm and PVI-Br, which were comparable to the theoretical compositions, except for the product obtained at the high $[M]_0/[\text{macro-CTA}]_0$ ratio ($[\text{PVI-Br}]_0/[\text{macro-CTA}]_0$ = 250). This may be due to the difficulty to evaluate the high molecular weights by using this spectroscopic method because of low signal-to-noise ratio of the peaks of each segment. Nevertheless, these results suggest that the composition of each segment and molecular weights of the resulting block copolymers could be adjusted by the $[\text{PVI-Br}]_0/[\text{macro-CTA}]_0$ ratio in the feed.

When the polymerization of EtOEVI-Br was carried out with the poly(NIPAAm) macro-CTA at $[M]_0/[\text{macro-CTA}]_0$ = 50 using the ratio of AIBN to macro-CTA of 1:2 ($[M]_0/[\text{CTA}]_0/[\text{AIBN}]_0$ = 100/2/1), the conversion determined by ^{1}H NMR spectroscopy was 57%, and the polymer was recovered by precipitation in acetone/diethyl ether (3/7 vol %). As can be seen in Figure 8a, the SEC chromatograms of the starting macro-CTA and the second-growth polymer show that the molecular weight clearly shifts to the higher molecular range, with polydispersity remaining M_w/M_n < 1.5. In the ^{1}H NMR spectrum of the block copolymer measured in CD_3OD, the peaks corresponding to both components are clearly detected (Figure 7b). A similar tendency was also observed in the polymerization of EHVI-Br with the poly(NIPAAm) macro-CTA. A shift in the SEC trace toward higher molecular weight region, with polydispersity remaining M_w/M_n < 1.4 (Figure 8b), clearly demonstrates the block formation. In this case, the SEC trace of the block copolymer is unimodal with relatively narrow molecular weight distribution (M_w/M_n = 1.39). These results indicate that chain extension from the dithiocarbonate-terminated poly(NIPAAm) to *N*-vinylimidazolium salts could be well controlled under suitable conditions and provided block copolymers with as-designed chain structures and relatively low polydispersities.

Thermal Phase Transition and Assembled Structure in Aqueous Solution. Dual-stimuli-responsive materials, such as temperature- and pH-sensitive polymers and gels, have recently attracted significant research interest because these dual functional systems have great importance in biological applications and can mimic the responsive macromolecules found in nature.[75−79] In particular, there is growing interest in developing dual-stimuli-responsive block copolymers since the ability to respond to external stimuli, such as pH, salt, and temperature, offers an additional control over hierarchical structures formed via self-assemblies. In this study, poly(*N*-vinylimidazolium salt) was selected as an ionic segment, and poly(NIPAAm) was employed as a thermo-responsive segment. Three poly(*N*-vinylimidazolium salt)s were soluble in methanol, DMSO, DMF, and chloroform and insoluble in ethyl acetate, THF, diethyl ether, and hexane, regardless of the structure of the substituent group. Note that only poly(EtOEVI-Br) was soluble in water, whereas poly(PVI-Br) and poly(EHVI-Br) were hard to dissolve in water. In addition to the structure of the substituent group on the imidazolium ring, the solubility and

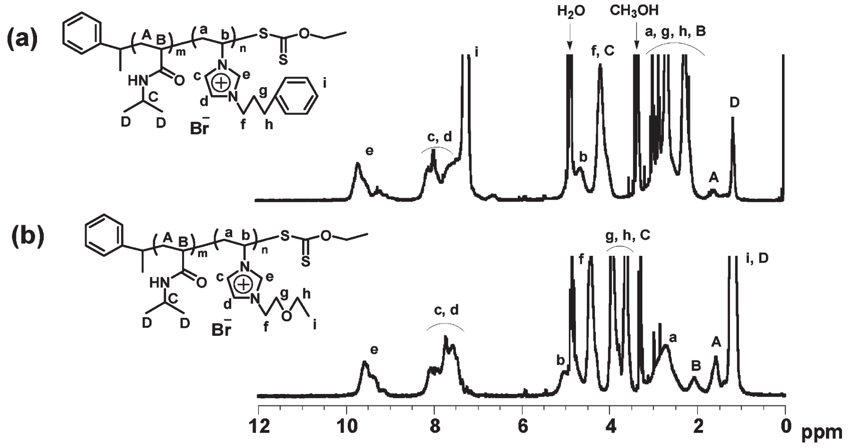


Figure 7. ^{1}H NMR spectra (CD_3OD) of (a) poly(NIPAAm)-*b*-poly(PVI-Br) and (b) poly(NIPAAm)-*b*-poly(EtOEVI-Br).

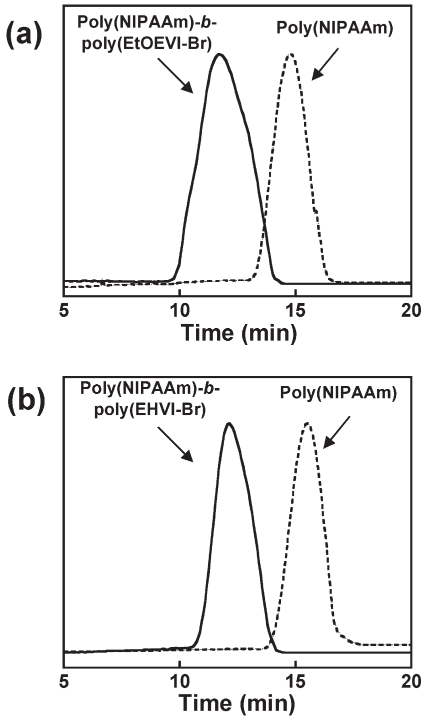


Figure 8. SEC traces of block copolymers (solid lines) obtained at [M]/[macro-CTA]/[AIBN] = 100/2/1 and parent poly(NIPAAm)s used as macro-CTAs (dotted lines): (a) poly(NIPAAm)-*b*-poly(EtOEVI-Br) ($M_{n,GPC}$ = 55 900 g/mol, M_w/M_n = 1.42, conv = 57%) and poly(NIPAAm) (M_n = 10 300 g/mol and M_w/M_n = 1.34); (b) poly(NIPAAm)-*b*-poly(EHVI-Br) ($M_{n,GPC}$ = 57 900 g/mol, M_w/M_n = 1.39, conv=60%) and poly(NIPAAm) (M_n = 6100 g/mol and M_w/M_n=1.31).

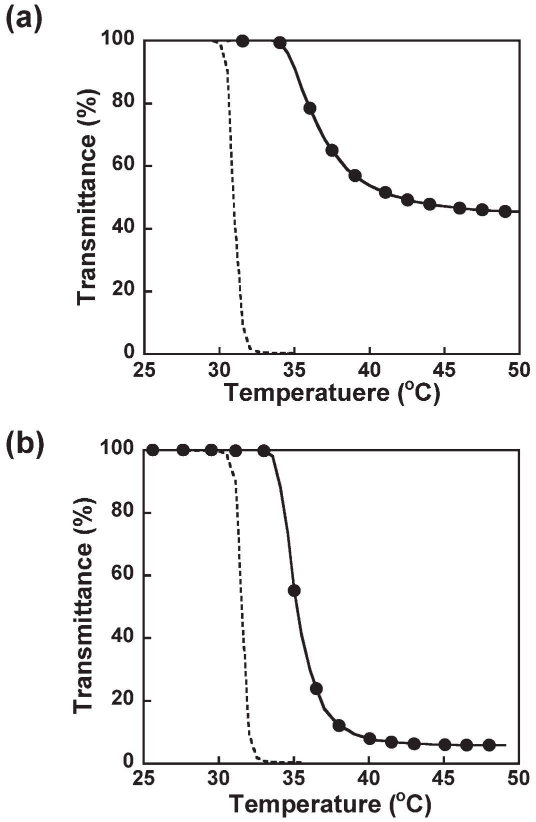


Figure 9. Temperature dependence of the transmittance at 500 nm in aqueous solutions (polymer concentration = 2.0 mg/mL, pH = 7) of (a) poly(NIPAAm)$_{27}$-*b*-poly(EtOEVI-Br)$_{73}$ (solid line, M_n = 55 900 g/mol, M_w/M_n = 1.42) and (b) poly(NIPAAm)$_{91}$-*b*-poly(PVI-Br)$_9$ (solid line, M_n = 18 400 g/mol, M_w/M_n = 1.46) and poly(NIPAAm) (dotted line).

various properties of the poly(*N*-vinylimidazolium salt)s are considered to be manipulated by the structure of counteranion. The pH value and salt concentration of aqueous solution may also affect characteristic solution behaviors. Poly(NIPAAm) is known to possess characteristic LCST (lower critical solution temperature)-type thermoresponsive property, which exhibits a soluble–insoluble transition at 32 °C in water. Hence, the block copolymers comprising poly(*N*-vinylimidazolium salt) and poly(NIPAAm) can be regarded as dual stimuli-responsive block copolymers with an ionic segment and a thermoresponsive segment.

We initially evaluated thermally induced phase separation behavior of poly(NIPAAm)$_{27}$-*b*-poly(EtOEVI-Br)$_{73}$ in water, as monitored by UV (500 nm), in which the heating rate was fixed at 1.0 °C/min. As can be seen in Figure 9, the double hydrophilic block copolymer is soluble in water at low temperature, and the transparent solution is gradually changed into turbid solution (transparency = 50% at 50 °C). This is an indication that the introduction of the ionic poly(EtOEVI-Br) segment leads to the increase in the transition temperature. The result is consistent with the general tendency that the LCST depends on the distribution of hydrophilic and hydrophobic groups within the polymers and that the transition temperature increases with increasing hydrophilicity. In contrast, the block copolymers containing poly(PVI-Br) or poly(EHVI-Br) were insoluble in water at

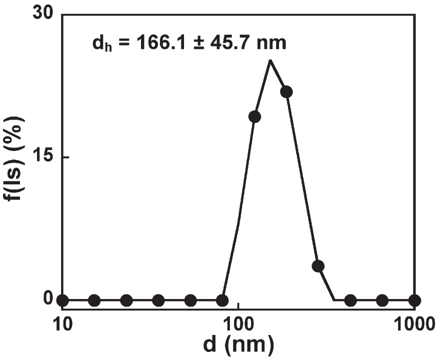


Figure 10. Hydrodynamic diameter distributions, *f*(D_h), of the micelle obtained from poly(NIPAAm)$_{91}$-*b*-poly(PVI-Br)$_{9}$ at 25 °C.

room temperature, which are due to the low solubility of poly(PVI-Br) and poly(EHVI-Br) in water. In terms of the water solubility, poly(NIPAAm)-*b*-poly(EHVI-Br) and poly(NIPAAm)-*b*-poly(PVI-Br) could be regarded as hydrophilic (thermoresponsive) and hydrophobic (ionic) block copolymers. In order to evaluate the thermoresponsive property and the assembled structures of these amphiphilic block copolymers, the water-soluble part was collected by filtration of the aqueous dispersion of poly(NIPAAm)$_{40}$-*b*-poly(PVI-Br)$_{60}$, which was stirred at room temperature. The resulting block copolymer having high NIPAAm content (poly(NIPAAm)$_{91}$-*b*-poly(PVI-Br)$_{9}$, $M_n = 18\,400$ g/mol, $M_w/M_n = 1.46$) was employed for the measurements. As shown in Figure 9b, the block copolymer was soluble in water at low temperature, which undergoes a clear phase transition from 33 to 38 °C upon heating. A clear phase transition from 100% at 30 °C to less than 10% at 45 °C is detected, and the transition temperature is slightly higher than that of poly(NIPAAm). These results suggest that the thermoresponsive behavior and transition temperature can be tuned by the structure of the substituent group on the poly(*N*-vinylimidazolium salt) segment and the comonomer composition.

The solution property of the amphiphilic block copolymer, poly(NIPAAm)$_{91}$-*b*-poly(PVI-Br)$_{9}$, was characterized using DLS in water, which is a good solvent only for poly(NIPAAm) at room temperature. As shown in Figure 10, the block copolymer shows a monomodal hydrodynamic diameter distribution (D_h = 166 nm) in the selective solvent at 25 °C. The relatively narrow hydrodynamic diameter distribution most probably indicates the formation of the micelles consisting of a relatively hydrophobic core of poly(PVI-Br) and a hydrophilic shell of poly(NIPAAm). In contrast, no detectable micelle formation was observed in the double hydrophilic block copolymer, poly(NIPAAm)$_{27}$-*b*-poly(EtOEVI-Br)$_{73}$, comprising a thermoresponsive segment and an ionic segment. Since various properties of ionic liquids can be tuned widely by adjusting the structure of the anion (e.g., halide, tetrafluoroborate, hexafluorophosphate), the characteristic thermoresponsive properties and ordered structures of the imidazolium-based block copolymers are considered to be manipulated by the anion exchange reactions. Further studies on the thermoresponsive properties and the assembled structures of the block copolymers having different counteranion, composition, and chain length under various conditions (different pH values and salt concentrations) are now in progress, which will be separately reported.

Conclusion

This work presented the controlled synthesis of poly(*N*-vinylimidazolium salt)s with narrow molecular weight distribution, predetermined molecular weight by RAFT polymerization. Using xanthate-type CTAs, the polymerization of *N*-vinylimidazolium salts proceeded in a controlled fashion, as confirmed by the molecular weight controlled by the monomer/CTA molar ratio, a linear increase in the number-average molecular weight with the conversion, and the ability to extend the chain by a second addition of the monomer. The structure of the substituent group on the imdazolium ring affected the polymerization behavior and solubilities of the resulting poly(*N*-vinylimidazolium salt)s. We believe that this paper represents the first report on controlled radical polymerization of *N*-vinylimidazolium salts, which can be regarded as ionic liquid monomers having characteristic *N*-vinyl structure. Well-defined thermoresponsive ionic liquid block copolymers were obtained by RAFT polymerization of *N*-vinylimidazolium salts using poly(NIPAAm) macro-CTA under suitable conditions. This work substantially broadens and extends the scope of the block copolymers containing poly(*N*-vinylimidazolium salt)s, in which precise control of the molecular weight, polydispersity, composition, and functions can be achieved using the controlled radical polymerization technique.

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Supporting Information Available: Figures showing NMR spectra of the chain transfer agents, monomers, and polymers, comparison of the polymerization kinetics at different [M]/[CTA] ratios, and tables summarizing the solubilities of the monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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