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Synthesis of polyvinyl alcohol stereoblock copolymer via the combination of living cationic polymerization and RAFT/MADIX polymerization using xanthate with vinyl ether moiety

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Abstract

Different types of novel xanthates containing a vinyl ether moiety, *S*-benzyl *O*-2-(vinylloxy)ethyl carbonodithioate (Xanthate 1) and *S*-1-(ethoxycarbonyl)ethyl *O*-2-(vinylloxy)ethyl carbonodithioate (Xanthate 2) were synthesized. In particular, the Xanthate 2 enabled to design polyvinyl alcohol (PVA) stereoblock copolymer via the combination of living cationic vinyl polymerization and RAFT/MADIX polymerization. For cationic polymerization of isobutyl vinyl ether (IBVE) and *tert*-butyl vinyl ether (TBVE), the polymerizations were conducted under Xanthate 1-HCl adduct/SnCl₄ and Xanthate 1 or 2-CF₃COOH adduct/EtAlCl₂ initiating system in the presence of ethyl acetate. Both systems proceeded in living polymerization fashion because the calculated M_n of both poly(IBVE) and poly(TBVE) matches with the M_n polymerized assuming that one polymer chain is formed per one molecule of the Xanthate 1 or 2. The resulting poly(TBVE) had a high number average α -end functionality as determined by MALDI-TOF-MS spectrometry. Xanthate 2 is more efficient for the following RAFT/MADIX polymerization of vinyl acetate (VAc). The RAFT/MADIX polymerization of vinyl acetate (VAc) using azobis(isobutyronitrile) (AIBN) at 60 °C was conducted using either poly(IBVE) or poly(TBVE) macro-CTA. The poly(TBVE) macro-CTAs synthesized from the Xanthate 2 were able to polymerize VAc smoothly via RAFT/MADIX polymerization, to prepare well-defined diblock copolymer, poly(TBVE)-*b*-poly(VAc). The resulting block copolymer was then hydrolyzed using KOH in methanol and followed by acid hydrolysis using HBr gas bubbling. The resulting polymer is inherently stereoblock like copolymer, isotactic rich PVA-*b*-atactic PVA (iPVA-*b*-aPVA). From the DSC measurement, the iPVA-*b*-aPVA has one glass transition at 69.5 °C and two melting points according to iPVA and aPVA at 237.9 and

198.1 °C, respectively. Thus, it can be suggested that the obtained PVA has two different geometries by the combination of living cationic polymerization and RAFT/MADIX polymerization.

1. Introduction

Living/controlled polymerization is the most versatile method to design and control precisely polymer structure. The resulting block copolymers are useful materials in many applications such as nanomaterials [1-3] including nanocarrier [4], thermoplastic elastomers [5], and photoresists [6]. These are generally synthesized by adding two or more monomers in the polymerization system of the same mechanism activity. In practice, it is difficult to synthesize well-defined block copolymers with different unsaturated monomers. In addition, as can be seen in ionic and coordination polymerization, only a few of controlled living polymerization can provide additional control for the products such as stereoregularity or perfect sequences.[7,8] To realize the control over both chain architecture and microstructure, many researchers have investigated the hybrid polymerization. The selectivity of the monomers becomes wider, and new functions and versatility for additional control are expected.

To date, many studies have been conducted on the mechanistic transformation from anionic to cationic, cationic to radical, radical to anionic and vice versa [9,10]. The combination of precision polymerization to produce novel block copolymers was first introduced by Burgess et. al. who combined living anionic polymerization of styrene (St) to living cationic ring-opening polymerization of tetrahydrofuran [11]. The mechanistic transformation of living polymerization of vinyl monomers was investigated by Matyjaszewski et. al., which involved the transformation reaction from

living cationic to controlled radical polymerization [12]. Recent developments of the living/controlled polymerization have enabled to combine different polymerization methods and prepare various copolymers with many architectures such as blocks, grafts and stars [13-19]. Among them, only a few studies focusing on the combination of living cationic polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization. Examples include transformation of living cationic vinyl polymerization to RAFT polymerization to synthesize poly(meth)acrylates-*block*-polyvinyl ether [20] and the site transformation of polyisobutylene chain ends into RAFT polymerization [21,22]. Furthermore, in the recent years, we also have reported some methods to prepare well-defined block copolymers between vinyl ethers and radically polymerizable monomers and controlled molecular weight involving two mechanism polymerizations, such as living cationic polymerization and RAFT polymerization [23-26]. Quite recently, we have successfully synthesized a novel vinyl ether-type RAFT agent, benzyl 2-(vinylloxy)ethyl carbonotrithioate (BVCT). The BVCT/EtAlCl₂ initiating system in the presence of ethyl acetate have enabled us to prepare the macro-chain transfer agents (macro-CTAs) of poly(vinyl ether) for the RAFT polymerization. The block copolymerizations of ethyl acrylate, styrene, and *N*-isopropylacrylamide via RAFT polymerization were successfully conducted using the poly(vinyl ether) macro-CTAs. However, non-conjugated monomer of vinyl acetate (VAc) cannot be polymerized [26].

In this study, we synthesized novel vinyl-ether type xanthates including a cationically polymerizable moiety and xanthate of a RAFT agent. In common, RAFT polymerization using such a xanthate is called as macromolecule design through interchange of xanthates (MADIX) [27-29]. The xanthate enables to synthesize novel

block copolymers consisting of cationically polymerizable vinyl ethers and radically polymerizable non-conjugated monomer, VAc. To the best of our knowledge, this is the first example of the combination of polymerization involving cationic polymerization and RAFT/MADIX polymerization.

In general, the RAFT/MADIX polymerization is useful for the polymerization of non-conjugated monomers such as *N*-vinyl carbazole, *N*-vinyl pyrrolidone and vinyl acetate. This is because the polymer radicals are very reactive and tend to add quickly to the activated C=S bond during the propagating reaction. As the result, the intermediate radical in the equilibrium during the RAFT process is relatively unstable. Therefore, a xanthate with a low reactivity of C=S bond allows the addition of poorly stabilized propagating radicals on the double bond and give some control over the molecular weight of the polymer through the MADIX process.

Herein, the combination of RAFT/MADIX and living cationic polymerization allows us to prepare PVA stereoblock copolymer. An isotactic-rich poly(TBVE) was inherently obtained from (living) cationic polymerization [30] while an atactic poly(VAc) was obtained from (RAFT) radical polymerization [27,31]. On this basis, we extended recent studies on mechanistic transformation (combination polymerization) involving living cationic polymerization and RAFT/MADIX polymerization to generate a novel block copolymer, poly(TBVE)-*b*-poly(VAc). As a typical example, the resulting block copolymer precursor, poly(TBVE)-*b*-poly(VAc) was then hydrolyzed to prepare a stereoblock copolymer of polyvinyl alcohol (PVA); isotactic rich PVA-*b*-atactic PVA (iPVA-*b*-aPVA).

PVA is a commodity polymer which was developed for applications in a general industrial material such as transparent film, adhesive and many more due to its

characteristics such as solubility in water, low toxicity and biodegradability [32-35]. Typically, PVA cannot be synthesized directly from vinyl alcohol monomer, but it is synthesized by hydrolysis of poly(VAc) prepared from radical polymerization. On the other hand, PVA also can be obtained by hydrolysis of poly(TBVE) prepared by living cationic polymerization [36,37]. The combined block copolymer can be obtained by the combination of living cationic polymerization and RAFT/MADIX polymerization, and the stereoregularity of the polymer is essentially controlled as shown in Scheme 1.

Scheme 1. Synthesis of iPVA-*b*-aPVA from poly(TBVE)-*b*-poly(VAc) via the combination of living cationic polymerization and RAFT/MADIX polymerization.

2. Experimental

2.1 Materials

Isobutyl vinyl ether (IBVE) (TCI; > 99.0%), and *tert*-butyl vinyl ether (TBVE) (Sigma Aldrich; >99.0%) were washed with aqueous alkaline solution and then with water. These monomers were distilled twice over calcium hydride and were stored in a brown ampule under dry nitrogen in refrigerator. Vinyl acetate (VAc) (TCI; > 99.0%) was distilled over calcium hydride and was stored in a brown ampule. For solvent, toluene (Wako; > 99.5%) was washed by the usual method and then was distilled over calcium hydride just before use. Ethyl acetate (Wako; > 99.5%) as an added base for living cationic polymerization was distilled twice over calcium hydride and was stored in a brown ampule under dry nitrogen. For Lewis acids, ZnCl_2 (Aldrich; 1.0 M solution in diethyl ether), EtAlCl_2 (Aldrich; 1.0 M solution in hexanes), and SnCl_4 (Aldrich; 1.0 M solution in dichloromethane) were used as commercially supplied. Dioxane (dehydrated, Wako; > 99.5%) for the solvent of RAFT/MADIX polymerization was used as commercially supplied. The initiator, 2,2'-azobis(isobutyronitrile) (AIBN; Wako) was recrystallized from diethyl ether and stored in refrigerator.

2.2 Synthesis of *S*-benzyl *O*-2-(vinylloxy) ethyl carbonodithioate (Xanthate 1) and *S*-1-(ethoxycarbonyl)ethyl *O*-2-(vinylloxy)ethyl carbonodithioate (Xanthate 2)

For Xanthate 1, in a three-neck round bottom flask equipped with a reflux, 3.6 g of 1,1'-thiocarbonyl diimidazole and 0.05g (20 mmol) of KOH was dissolved in 60 ml toluene. 1.9 mL (20 mmol) of 2-hydroxyethyl vinyl ether (HOVE, donated by Maruzen Petrochemical) was then added and stirred. The mixture was heated at 60 °C for about 6 hours and left overnight at room temperature with stirring. *O*-2-(vinylloxy)ethyl

1*H*-imidazole-1-carbothioate was synthesized during this process. 2.4 mL (20 mmol) of benzyl mercaptan was then added and stirred. The mixture was then continue to heat at 60 °C for about 6 hours and left overnight at room temperature with stirring. The suspension was filtrated, and the excess toluene was removed by an evaporator. The product was then isolated from residue by column chromatography, using silica gel as stationary phase, with mixture of ethyl acetate and hexane as an eluent (1:10 v/v). The solvent was evaporated to dryness and the yellow product was verified using ¹H NMR, ¹³C NMR, and IR spectroscopy (yield: 60%). ¹H NMR (CDCl₃, 25 °C): δ 4.08 and 4.21 (dd, 2H, CH₂CHO, *J* = 2.38 and 2.37 Hz), 6.50 (q, 1H, CH₂CHO, *J* = 6.87 Hz), 4.83 (t, 2H, CH₂CH₂O, *J* = 4.65 Hz), 4.03 (t, 2H, CH₂CH₂O, *J* = 4.65 Hz), 4.38 (s, 2H, CS₂CH₂C₆H₅), 7.23-7.38 (m, 5H, CS₂CH₂C₆H₅). ¹³C NMR (CDCl₃, 25 °C): δ 40.26, 64.8, 71.12 (all CH₂), 87.10 (OCHCH₂), 127.30 (phenyl-C₄), 128.34 (phenyl-C₂), 128.79 (phenyl-C₃), 135.27 (phenyl-C₁), 150.98 (OCHCH₂), 213.41 (CO(S)S). IR (neat, r.t.): 1065, 1191, 1495, 1616 cm⁻¹.

For Xanthate 2, the intermediate process is the same as Xanthate 1 where *O*-2-(vinylloxy)ethyl 1*H*-imidazole-1-carbothioate was yielded. 2.6 mL (20 mmol) of ethyl 2-mercaptopropionate was then added and stirred. The mixture was then continue to heat at 60 °C for about 6 hours and left overnight at room temperature with stirring. The suspension was filtrated, and the excess toluene was removed by an evaporator. The product was then isolated from residue by column chromatography, using silica gel as stationary phase, with mixture of ethyl acetate and hexane as an eluent (1:5 v/v). The solvent was evaporated to dryness and the yellow product was verified using ¹H NMR, ¹³C NMR, and IR spectroscopy (yield: 65%). ¹H NMR (CDCl₃, 25 °C): δ 4.01 (dd, 2H, CH(H)CHO, *J* = 2.37 Hz), 4.17 (d, 1H, CH(H)CHO, *J* = 2.46 Hz), 6.42 (q, 1H,

CH₂CHO, $J = 6.79$ Hz), 4.73 (t, 2H, CH₂CH₂O, $J = 4.55$ Hz), 3.97 (t, 2H, CH₂CH₂O, $J = 4.62$ Hz), 4.32 (q, 1H, CS₂CHCH₃, $J = 7.33$ Hz), 1.52 (d, 3H, CS₂CHCH₃, $J = 7.48$ Hz), 4.14 (q, 2H, OCH₂CH₃, $J = 6.94$ Hz), 1.22 (t, 3H, OCH₂CH₃, $J = 7.12$ Hz). ¹³C NMR (CDCl₃, 25 °C): 61.53, 64.78, 71.40 (all CH₂), 13.89, 16.72 (all CH₃), 47.21 (CS₂CHCH₃), 87.13 (CH₂CHO), 151.03 (CH₂CHO), 170.80 (CO₂CH₂CH₃), 211.89 (CS₂CHCH₃). IR (neat, r.t.): 1064, 1193, 1374, 1617, 1734 cm⁻¹.

2.3 Synthesis of macro-RAFT agents.

For Xanthate 1/HCl/ZnCl₂ and Xanthate 1/HCl/SnCl₄ based initiating system, the Xanthate 1-HCl adduct was synthesized just before use via the reaction of the Xanthate 1 in toluene solution with hydrogen chloride gas generated from sulfuric acid and sodium chloride. All of the apparatus were baked at 250 °C for 10 min before use. Cationic polymerization was carried out at 0 °C under a dry nitrogen atmosphere in a Schlenk tube equipped with a three-way stopcock baked at 250 °C for 10 min before use. The cationic polymerization was conducted as follows: [IBVE]₀ = 0.3 M, [Xanthate 1]₀ = 5.0 mM, [Lewis acid]₀ = 1.0 mM. Toluene (1.8 mL), IBVE (0.2 mL, 0.095 mmol), and 10 mM of Xanthate 1-HCl in toluene solution (2.5 mL) were added into the glass tube using dry medical syringes, successively. The polymerization was initiated by the addition of a prechilled 10 mM Lewis acid in toluene solution (0.5 mL) at 0 °C. After the desired time, the reaction was terminated with prechilled methanol (0.5 mL) containing a small amount of aqueous ammonia solution (0.1 wt%). The quenched mixture was diluted in either hexane or dichloromethane and was successively washed with 0.1 mol/L hydrochloric acid, water, 0.1 mol/L aqueous NaOH solution, and water to remove the initiator residues. The volatiles were then removed under reduced

pressure over 50 °C, and the residue was vacuum-dried for a day at room temperature. The monomer conversion was determined by gravimetry.

For Xanthate 1 or 2/trifluoroacetic acid (TFA) adduct/ EtAlCl_2 based initiating system, the Xanthate 1 or 2-TFA adduct was synthesized as follows. All of the apparatus were baked at 250 °C for 10 min before use. First, in two necks round bottom flask, 0.1 mL of Xanthate 1 (or 2) was added using medical syringe. Then, 11.7 mL (11.5 mL for Xanthate 2) of toluene was added into the flask to prepare 40 mM Xanthate in toluene solutions. These solutions were dehydrated over CaCl_2 for 3 hours at 0 °C with stirring and then filtered under N_2 atmosphere. Using the Xanthate in toluene (stock solution), 20 mM Xanthate-TFA solutions were prepared in a Schlenk tube. The cationic polymerization was conducted as follows: $[\text{IBVE or TBVE}]_0 = 0.38 \text{ M}$, $[\text{Xanthate 1 or 2}]_0 = 5.0 \text{ mM}$, $[\text{TFA}]_0 = 5.0 \text{ mM}$, $[\text{EtAlCl}_2]_0 = 10 \text{ mM}$, $[\text{Ethyl Acetate}] = 1.0 \text{ M}$. Toluene (2.5 mL), ethyl acetate (0.50 mL, 5.1 mmol), IBVE (0.25 mL, 0.095 mmol), and 20 mM of Xanthate-TFA in toluene solution (1.25 mL) were added into the glass tube using dry medical syringes, successively. The polymerization was initiated by the addition of a prechilled 10 mM Lewis acid in toluene solution (0.5 mL) at 0 °C. After the desired time, the reaction was terminated with prechilled methanol (0.5 mL) containing a small amount of aqueous ammonia solution (0.1 wt%). The quenched mixture was diluted in either hexane or dichloromethane and was successively washed with 0.1 mol/L hydrochloric acid, water, 0.1 mol/L aqueous NaOH solution, and water to remove the initiator residues. The volatiles were then removed under reduced pressure over 50 °C, and the residue was vacuum-dried for a day at room temperature. The monomer conversion was determined by gravimetry.

2.4 RAFT/MADIX polymerization procedures

Either poly(IBVE) or poly(TBVE) macro-CTA with a predetermined *DP* (degree of polymerization) obtained by living cationic polymerization was mixed with AIBN and varying amount of VAc in a Schlenk tube. These were then diluted in bulk or solution such as toluene or dioxane for the desired concentration in a Schlenk tube equipped with a magnetic stir bar. For example, the typical contents for the polymerization of VAc were as follows: toluene (8.22 g, 32 mmol), VAc (0.42 mL, 5.3 mmol), poly(IBVE) macro-CTA (0.5 g, 23.5 μ mol, *DP* = 53), AIBN (3 mg, 5.3 μ mol); [VAc]₀/[poly(IBVE) macro-CTA]₀/[AIBN]₀ = 200:1:0.2 molar ratio; monomer conc. = 15 wt%. After three freeze-thaw-pump cycles, the flask was filled with nitrogen and sealed. Then, each polymerization was allowed to proceed at 60 °C and quenched after the desired time via cooling in ice water and exposure to air. The volatiles were then removed under reduced pressure over 40 °C, and the residue was vacuum-dried for a day at room temperature. The *DP* of the polymer was verified by ¹H NMR spectroscopy.

2.5 Synthesis of stereoblock copolymers

For alkaline hydrolysis, 0.125 g of poly(TBVE)-*b*-poly(VAc) and 12 mL methanol was added into a round bottom flask, and stirred with magnetic bar. 0.24 g of KOH was added into the flask and allowed to react for a day at room temperature. The volatiles were then removed under reduced pressure using rotary evaporator. After evaporation, residues were then removed by dialysis against deionized water using semipermeable cellulose tubing (SPECTRA/POR, corresponding to a molecular weight cutoff of 1000 Da) for two days followed by lyophilization.

For acid hydrolysis, the polymer in toluene solution (0.1 wt%) was reacted to

hydrogen bromide gas generated from sulfuric acid and sodium bromide. The excess hydrogen bromide gas was removed using nitrogen gas. The product was neutralized with 0.1 % ammonia in methanol, followed by washing three times with methanol and dried under reduced pressure at 30 °C.

2.6 Polymer Characterization

Molecular weight distributions (MWDs) were assessed by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 40 °C using three polystyrene gel columns [TSK gel G-MH_{HR}-M $\times$ 3 (exclusion limit: 4×10^6 (PSt)); 7.8 mm i.d. $\times$ 300 mm each; flow rate 1.0 mL/min] connected to a Tosoh CCPMII pump and an RI-8020 and UV-8020 for refractive index (RI) and ultraviolet (UV) detector, respectively. The RI detector was mainly used for determination of number-average molecular weight (M_n) and the polydispersity (M_w/M_n). For PVA, assessed by GPC in water containing 0.2 M NaNO₃ and 0.01 M NaH₂PO₄ (pH = 7) at 40 °C using two hydrophilic methacrylate gel columns [TSK gel α -M $\times$ 2 (exclusion limit: $> 10^7$ (PEO)); 7.8 mm i.d. $\times$ 300 mm each; flow rate 1.0 mL/min] connected to a Tosoh CCPS pump and an RI-8020 and UV-8020 for RI and UV detector, respectively. The M_n s of PVAs were calibrated by poly(ethylene oxide) (PEO). Thus, observed M_n s are larger than those calculated. The ¹H NMR spectra to determine the detailed structure and the compositions of block copolymers were recorded on either JEOL JNM-EX300 (300 MHz) or JEOL JNM-EX500 spectrometer (500 MHz). Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF-MS) spectra were recorded to determine the number-average end functionality of the RAFT terminal (F_n) using a Bruker Daltonics autoflex spectrometer (reflectron mode) using dithranol as the matrix and sodium

trifluoroacetate as the ion source (polymer sample/dithranol/sodium trifluoroacetate = 1/8/1 weight ratio). Differential scanning calorimetry (DSC) thermograms were recorded for glass transition temperature (T_g) and melting point (T_m) by means of Thermo Plus Evo II (Rigaku) at a rate of 5.0 °C/min on heating and cooling scans between 0 and 300 °C.

3. Results and discussion

3.1 Synthesis of xanthates

First, two novel xanthates containing a vinyl ether moiety were synthesized. Scheme 2 shows the synthesis of vinyl ether-type xanthates. Both xanthates were prepared from 2-hydroxyethyl vinyl ether (HOVE) and *O*-2-(vinylloxy)ethyl 1,1'-thiocarbonyl diimidazole (TCDI) [38]. Then the resulting *O*-2-(vinylloxy)ethyl 1*H*-imidazole-1-carbothioate reacted with the corresponding thiols to prepare Xanthate 1 and 2, respectively. Fig. 1 shows ^1H NMR spectra for both xanthates. For both xanthates, all the signal peaks are appeared, and the signal peaks (**c** and **c'**) ascribed for vinyl group at the terminal end are exhibited around 6.4 ppm. This indicates that both vinyl ether-type xanthates did not self-polymerized under the conditions and were successfully synthesized. Both xanthates were yielded over 60% and quantitatively synthesized as determined by ^1H NMR, ^{13}C NMR, and IR spectroscopies.

Scheme 2. Synthesis of Xanthate 1 and Xanthate 2 from HOVE.

Fig. 1. ^1H NMR spectra of (A) Xanthate 1 and (B) Xanthate 2 in CDCl_3 at 25 °C. The insets show their chemical structures with full peak assignments. Asterisks indicate solvent peaks for H_2O and toluene.

3.2 Living cationic polymerization of vinyl ether

The living cationic polymerizations of IBVE and TBVE were examined by using either Xanthate 1 or 2 of RAFT agents as an initiator with a Lewis acid including ZnCl_2 , SnCl_4 and EtAlCl_2 . Table 1 summarizes the polymerization result. All polymerizations of IBVE and TBVE were carried out in toluene in the presence of ethyl acetate as an additive (except for ZnCl_2) at 0 °C using a xanthate and Lewis acid with the following concentration: $[\text{monomer}]_0 = 0.38 \text{ M}$; $[\text{Xanthate}]_0 = 5.0 \text{ mM}$, $[\text{Lewis acid}]_0 = 10 \text{ mM}$, $[\text{ethyl acetate}] = 1.0 \text{ M}$. First, the living polymerization of IBVE was investigated under Xanthate 1-HCl/ ZnCl_2 initiating system. As a result, the polymerization is uncontrolled and a polymer with broad molecular weight distribution was obtained. This is due to the slow interconversion between the dormant species and active species. Next, we examined the living cationic polymerizations of IBVE and TBVE under Xanthate 1-HCl/ SnCl_4 initiating system in the presence of ethyl acetate (entry 2) and Xanthate 1 or 2-TFA/ EtAlCl_2 initiating system in the presence of ethyl acetate (entries 3-8). In detail, Xanthate 1 and 2 were used for entries 2-4 and entries 5-8 as an initiating species, respectively. From all of the polymerizations in entries 2-8, the livingness was observed for both polymerization systems of both monomers, IBVE and TBVE.

Table 1.

Living cationic polymerization results of alkyl vinyl ethers, IBVE and TBVE using either Xanthate 1 or 2 acid adducts.

Entry	Initiator ^b	Lewis acid	Monomer	Temp. (°C)	Time	Conv. (%)	M_n^c	M_w/M_n^c
1 ^a	X1-HCl	ZnCl ₂	IBVE	0	7 min	trace	-	-
2	X1-HCl	SnCl ₄	IBVE	0	15 min	100	5400	1.08
3	X1-TFA	EtAlCl ₂	IBVE	0	9 h	86.6	4700	1.12
4	X1-TFA	EtAlCl ₂	TBVE	-30	20 min	83.3	4000	1.29
5	X2-TFA	EtAlCl ₂	IBVE	0	2 h	42.3	2600	1.20
6 ^d	X2-TFA	EtAlCl ₂	TBVE	-15	4 h	100	7900	1.29
7	X2-TFA	EtAlCl ₂	TBVE	-30	30 min	84.9	4700	1.34
8	X2-TFA	EtAlCl ₂	IBVE	0	10 h	88.6	5400	1.13

^a In the absence of ethyl acetate.

^b The individual Xanthate 1 and Xanthate 2 are denoted by X1 and X2. The HCl and trifluoroacetic acid (TFA) adduct for the Xanthates are also denoted by -HCl and -TFA, respectively. Cationic polymerization conditions: [monomer]₀ = 0.38 M, [Xanthate acid adduct]₀ = 5.0 mM (i.e. [Xanthate]₀ = 5.0 mM, [HCl or TFA]₀ = 5.0 mM), [Lewis acid]₀ = 10 mM, [ethyl acetate] = 1.0 M in toluene.

^c Determined by GPC (polystyrene calibration).

^d [Xanthate 2-TFA]₀ = 2.5 mM

Fig. 2A shows the time-conversion curves for the polymerization of IBVE and TBVE for entries 2, 5 and 7. For the polymerization of TBVE using Xanthate 2-TFA/EtAlCl₂ initiating system (corresponding to entry 7), the polymerization proceeded without the induction phase and completed within 1 h. However, the polymerization of IBVE (corresponding to entries 5 and 8) was much slower than that of TBVE. This indicates the reactivity of TBVE is higher than that of IBVE. When SnCl₄ was used as Lewis acid instead of EtAlCl₂, the polymerization of IBVE progressed rapidly. Figure 2B shows the M_n and M_w/M_n values for the product polymers. The M_n s of both poly(IBVE) and poly(TBVE) increased in a direct proportion to the monomer conversion and the

resulting MWDs of poly(TBVE) are broader than those of poly(IBVE). The calculated M_n s for poly(IBVE) and poly(TBVE) are in good agreement with the M_n s polymerized from the used Xanthate assuming that one polymer chain is formed per one molecule of the Xanthate. Thus, both Xanthate 1 and 2 are useful for initiating species for the living cationic polymerization. However, due to the reactivity of TBVE which is higher than that of IBVE, therefore, the MWDs of poly(TBVE) are larger than those of poly(IBVE). Thus, all the polymerizations of poly(TBVE) were carried out below -15 °C to suppress the side reactions. Fig. 3A and Fig. 3B shows typical MWD curves for poly(IBVE) and poly(TBVE), respectively. The MWDs for both poly(IBVE) and poly(TBVE) are clearly shifted toward the higher molecular weights as monomer conversion increases.

Fig. 2. (A) Time-conversion curves for the polymerization of IBVE (○, ▲) and TBVE (●) for entries 2, 5 and 7, respectively. The polymerization of entry 5 proceeded up to 88.6% conversion for 10 h (see, entry 8 in Table 1). (B) M_n and M_w/M_n as a function of monomer conversion for IBVE (○, □) and TBVE (●, ■) for entries 2 and 7, respectively.

Fig. 3. Typical MWD curves for (A) poly(IBVE) (entry 2) and (B) poly(TBVE) (entry 7).

The representative ^1H NMR spectrum of the resulting poly(TBVE) is shown in Fig. 4. The polymer exhibited the signals ascribed to the Xanthate 2 (**d-k**) (i.e. α -end) and protons due to TBVE repeating units (**a-c**). Furthermore, the peaks for leaving group in

RAFT process (**h-k**) remains in poly(TBVE). This indicates that the poly(TBVE) possesses the RADIX/MADIX polymerization moiety, which is stable during living cationic polymerization process. For the poly(IBVE) with a Xanthate 1 moiety (see Fig. S1 in Supporting information), the signals ascribed to the Xanthate 1 and protons due to IBVE repeating units were also exhibited. Although M_n is agreement with the calculated from the used Xanthate and the α -end was clearly appeared from ^1H NMR spectroscopy, however, it is difficult to calculate the accurate number average end functionality (F_n) because ω -end does not clearly appeared. To calculate F_n in detail, MALDI-TOF-MS spectrum was measured. The F_n is an important value that has an influence on the efficiency of the block copolymer [23,24,26].

Fig. 4. Typical ^1H NMR spectrum of poly(TBVE) (entry 7) in CDCl_3 . Asterisks indicate solvent peaks for H_2O , toluene, and methanol.

The MALDI-TOF-MS spectroscopy analysis for the poly(TBVE) and poly (IBVE) macro-CTA was conducted to analyze both terminal end structures (α and ω -ends). Fig. 5 shows the MALDI-TOF-MS spectrum for poly(TBVE) ($M_n = 2600$, $M_w/M_n = 1.39$, see Fig. 3B) and the estimated chemical structures for each peak. Three major peaks were exhibited, where each peak is separated by 100 mass units, corresponding to the molar mass of TBVE repeating unit. Fortunately, the peak **a** shows clearly the structure of poly(TBVE) initiated from the Xanthate 2 was still remained, where, the experimental signal (1220.3 g/mol) fits the calculated molecular weight of poly(TBVE) with Xanthate 2 α -end, methoxy ω -end and Na^+ (1220.8 g/mol, $n = 9$). The peak **b** is corresponds to two types of poly(TBVE) and cannot be distinguished, i.e decomposed poly (TBVE) with Xanthate 2 α -end during the measurement (1156.4 g/mol, $n = 10$) and poly(TBVE) with proton initiating terminal derived from adventitious water or an excess TFA (1156.4 g/mol, $n = 11$). The peak **c** is ascribed to the poly(TBVE) with proton initiating terminal and quenching with *tert*-butyl alcohol triggered by adventitious water (1200.4 g/mol, $n = 11$). On the basis of these results, without the proton initiating terminal, the apparent intensity area ratio of the peaks **a** and **b** derived from the xanthate end group (α -end group) to the whole peaks is calculated to be approximately 0.94. However, if the polymerization was proceeded from a proton, the F_n is about 0.35, indicating that 35% of the polymer from the proton. Based on the Fig. 2B, the M_n of the polymers was definitely closed to the calculated values. This means that the polymerization proceeded with relatively high F_n from Xanthate 2 for the poly(TBVE) macro-CTA as expected.

Fig. 5. MALDI-TOF-MS spectrum of poly (TBVE) (entry 7) ($M_n = 2600$, $M_w/M_n = 1.39$). The detailed structures with their molecular weights and number repeating unit are calculated. The interpeak distances between the same structures correspond to the mass of TBVE repeating unit.

3.3 Synthesis of block copolymer via RAFT/MADIX polymerization

RAFT/MADIX polymerizations of VAc were conducted using the obtained macro-CTA by living cationic polymerization. The RAFT agent with a xanthate structure is generally suitable to the non-conjugated monomers such as VAc. [27-29, 39,40]. The RAFT/MADIX polymerization was conducted by using AIBN as an initiator at 60 °C in solvent or bulk with molar ratio of $[VAc]_0:[CTA]_0:[AIBN]_0 = 200-600:1:0.2-05$. Table 2 summarizes the results of the RAFT/MADIX polymerization. Entries 9 and 10 show the polymerization using the poly(IBVE) with Xanthate 1 as a macro-CTA obtained from the polymerization using $SnCl_4$. From the results, they have no increases in the molecular weight, and the polymerization is either very slow or does not proceed at all. Thus, the RAFT/MADIX polymerizations of VAc using Xanthate 1 and 2 were conducted as a model polymerization. The xanthates were treated with hydrochloric acid prior to radical polymerization because vinyl ether moiety can be partly radically-polymerized. In practice, the model Xanthate compounds were preliminarily synthesized by the reaction of equivalence ratio of Xanthate 1 or 2 and 1.0 M HCl in diethyl ether followed by water. The reactions provided ethyl *S*-benzyl *O*-(2-hydroxyethyl) carbonodithioate (HX-1) and *S*-1-(ethoxycarbonyl)ethyl *O*-2-(2-hydroxyethyl) carbonodithioate (HX-2) from Xanthate 1 and 2, respectively. For HX-2, it is shown that when protonic acid was added to Xanthate 2, the vinyl group peak at 6.4 ppm disappeared in Fig. 6B. The RAFT/MADIX polymerization of VAc in bulk was conducted at 60 °C using AIBN. For HX-2, polymerization of VAc proceeded. The obtained polymer exhibited the signals ascribed to the HX-2 (**a'-f'**) and VAc repeating units (**g'-i'**) in Fig. 6A. However, no polymerization occurred for HX-1. This

indicates that it is difficult for the benzyl group of free radical leaving group to initiate the polymerization of VAc in RAFT process. This is because of the stabilized benzyl radical derived from HX-1 by resonance. While, unstable ethoxycarbonyl ethyl radical derived from HX-2 can initiate the polymerization of VAc. Therefore, macro-CTA by living cationic polymerization from Xanthate 2 is suitable to the following RAFT/MADIX polymerization of VAc.

Table 2.

RAFT/MADIX polymerization of VAc at 60 °C using either poly(TBVE) or poly(IBVE) macro-CTA^a

Entry	macro-CTA ^b	[VAc] ₀ : [CTA] ₀ : [AIBN] ₀	Solvent	Conc. (wt %) ^c	Conv. (wt %)	M_n^d	M_w/M_n^d
9	X1-IBVE ₅₃	200 : 1 : 0.2	toluene	15	trace	-	-
10	X1-IBVE ₅₃	200 : 1 : 0.5	bulk	-	trace	-	-
11 ^e	X2-IBVE ₂₃	200 : 1 : 0.5	toluene	15	5.0	2800 (2600)	1.44 (1.39)
12	X2-IBVE ₂₃	200 : 1 : 0.5	dioxane	15	5.0	5400 (2600)	1.13 (1.39)
13	X2-TBVE ₇₆	200 : 1 : 0.2	bulk	-	64.0	16500 (7900)	1.27 (1.29)
14	X2-TBVE ₄₈	400 : 1 : 0.2	bulk	-	61.9	31100 (5200)	1.50 (1.27)
15	X2-TBVE ₄₂	600 : 1 : 0.2	bulk	-	60.8	75000 (5000)	1.90 (1.28)

^a Polymerization for 50 h.

^b The segment DP_n in the formula determined by GPC spectroscopy.

^c Monomer concentration in polymerization.

^d Determined by GPC (polystyrene calibration). The parenthetic value indicates the M_n and M_w/M_n for the corresponding macro-CTA.

^e Polymerization for 26 h.

Fig. 6. ^1H NMR spectra of (A) poly(VAc) using HX-2 and (B) HX-2 as a RAFT agent in CDCl_3 . RAFT/MADIX polymerization condition of poly(VAc): $[\text{VAc}]_0:[\text{HX-2}]_0:[\text{AIBN}]_0 = 400:1:0.2$. in bulk at 60°C . Asterisks indicate solvent peaks for toluene.

Entries 11-15 in Table 2 show the polymerization results using the poly(TBVE) macro-CTA with Xanthate 2. The polymerizations of VAc via RAFT/MADIX for entries 11-15 were conducted either in the presence of organic solvent or in bulk. For the polymerization in toluene or dioxane, monomer concentration was adjusted to 15 wt%. In dioxane, the polymerization of VAc proceeded. In the case of bulk polymerization, the M_n increased larger than those of the polymerization in a solvent. The comparison between entries 14 and 15 shows that 1.5 times higher concentration of VAc for the same macro-CTA provided a polymer with ca. 1.5 times higher M_n . This indicates that the RAFT/MADIX polymerization of VAc proceeded in controlled fashion.

Fig. 7 shows the typical GPC result and the ^1H NMR spectrum for poly(TBVE)-*b*-poly(VAc) (entry 14). In Fig. 7A, the MWD of poly(TBVE)-*b*-poly(VAc) clearly shifted toward the higher molecular weights relative to that of poly(TBVE) macro-CTA and was relatively narrow even after block copolymerization. At the higher molecular weight, the polymer is obtained via RAFT/MADIX polymerization using the poly(TBVE) macro-CTA while the tailing is likely to be unreacted poly(TBVE) homopolymer. Furthermore, the M_w/M_n value become larger with increasing amount of VAc against poly(TBVE). In particular, MWD of block copolymer (entry 15) is broader and the initiating efficiency was poor. Therefore, it can be assumed that the optimum condition for poly(TBVE)-*b*-poly(VAc) is in bulk and the molar ratio is $[\text{VAc}]_0/[\text{CTA}]_0 \leq 400$.

To confirm the block copolymerization in detail, the ^1H NMR spectrum of poly(TBVE)-*b*-poly(VAc) was recorded in Fig. 7B. All peaks attributed to TBVE (**a-c**) and VAc units (**d-f**) were exhibited in d_6 -DMSO. The composition was calculated to be TBVE₄₈-*b*-VAc₂₀₆ by ^1H NMR spectrum, which is in good agreement with that estimated by conversion. Thus, it is suggested that poly(TBVE)-*b*-poly(VAc) block copolymer was successfully synthesized.

Fig. 7. RAFT/MADIX polymerization of VAc using poly(TBVE) macro-CTA (entry 14) in bulk at 60 °C: [VAc]₀/[poly(TBVE)]₀/[AIBN]₀ = 400:1:0.2. (A) Typical GPC curves of poly(TBVE)-*b*-poly(VAc) and the corresponding poly(TBVE) macro-CTA. (B) ¹H NMR spectrum of the resulting poly(TBVE)-*b*-poly(VAc) in *d*₆-DMSO. Asterisks indicate solvent peaks for toluene and H₂O.

3.4 Synthesis of PVA stereoblock copolymer

The hydrolysis of homopolymers, poly(TBVE) and poly(VAc), were conducted. Poly(VAc) was hydrolyzed by using KOH in methanol to obtain PVA. Fig. 8A shows the ^1H NMR result of PVA. In d_6 -DMSO, the signals attributed to the PVA polymer were confirmed. From the signal peak of hydroxyl group at 4.2 ppm, the dyad tacticity (%) = 46.0 (meso), and 54.0 (racemo). This indicates that the atactic polymer was obtained. On the other hand, poly(TBVE) was hydrolyzed by using HBr. From ^1H NMR spectra result in Fig. 8B, all of the signal peaks ascribed to the PVA were exhibited including *tert*-butyl alcohol caused by the hydrolysis. The percentages of meso (m) and racemo (r) of PVA from poly(TBVE) are 70.4 and 29.6, respectively. Thus, the isotactich rich PVA can be obtained from the hydrolysis of poly(TBVE).

Fig. 8. ^1H NMR spectra of PVA in d_6 -DMSO (a) PVA obtained from poly(VAc) by hydrolysis using KOH in methanol. RAFT/MADIX polymerization was conducted in bulk at 60 °C: $[\text{VAc}]_0:[\text{HX-2}]_0:[\text{AIBN}]_0 = 400:1:0.2$. (Polymerization time = 50 h, conv. ~60%, $M_n = 25000$, $M_w/M_n = 1.40$). (b) PVA obtained from poly(TBVE) by hydrolysis using HBr bubbling. Living cationic polymerization condition in toluene at -30 °C: $[\text{TBVE}]_0 = 0.38$ M, $[\text{Xanthate 2}]_0 = 5.0$ mM, $[\text{TFA}]_0 = 5$ mM, $[\text{EtAlCl}_2]_0 = 10.0$ mM, $[\text{ethyl acetate}]_0 = 1.0$ M. (Polymerization time = 60 min, conv. ~100%, $M_n = 5200$, $M_w/M_n = 1.27$).

The resulting poly(TBVE)-*b*-poly(VAc) of entry 14 in Table 2 was then hydrolyzed using KOH in methanol to prepare poly(TBVE)-*b*-PVA block copolymer. For the triad tacticity, the percentages of isotactics, heterotactics and syndiotactics are I: 26.9, H: 48.9, S: 24.2, respectively, and for the dyad tacticity, the percentages of meso and racemo form are m: 51.4, r: 48.6, respectively. Although all the VAc units of poly(TBVE)-*b*-poly(VAc) were saponified, the TBVE moieties in

poly(TBVE)-*b*-poly(VAc) can be partly converted into PVA by the alkaline hydrolysis. Thus, the resulting polymer changed to be slightly meso-rich relative to PVA prepared by the hydrolysis of PVAc homopolymer. Hence, this indicates that poly(TBVE)-*b*-PVA are containing atactic PVA by hydrolysis.

To prepare a PVA stereoblock copolymer, the resulting poly(TBVE)-*b*-PVA was further hydrolyzed using HBr gas bubbling. The resulting polymer can dissolve in water after hydrolysis. Fig. 9 shows the GPC result using aqueous eluent (pH = 7) for the final block copolymer, i.e. PVA stereoblock copolymer (A). The MWD clearly shifted toward the higher molecular weights relative to PVA hydrolyzed from the poly(TBVE) macro-CTA (C) even though the MWD after the hydrolysis is broader than that of the protected polymer (see Table 2 and Fig. 7A). In addition, the MWD is further shifted toward the higher molecular weights relative to PVA hydrolyzed from the corresponding poly(VAc) segment (B) shown in Fig. 6A. This result indicates that the block copolymer structure still intact even after hydrolysis. Thus, PVA stereoblock copolymer is not the mixture of the homopolymers. Although the precursor poly(TBVE)-*b*-poly(VAc) possesses a xanthate group, the xanthate group is protected and stable thanks to the solubility control during the course of hydrolysis (the illustration is shown in Fig S2 in Supporting information). During the alkaline hydrolysis of the resulting poly(TBVE)-*b*-PVAc, only poly(VAc) block is dissolved in methanol, whereas the poly(TBVE) block and xanthate moiety is insoluble in methanol. This means only the poly(VAc) block is hydrolyzed into PVA and the resulting product is then precipitated. The similar process was conducted against acid hydrolysis in toluene to obtain the final product, iPVA-*b*-aPVA. However, there is always the possibility of the cleavage of xanthate moiety. Thus, such a suitable deprotection condition is necessary to obtain the

stereoblock copolymer through hydrolysis.

Fig. 9. GPC curves of (A) iPVA-*b*-aPVA hydrolyzed from poly(TBVE)-*b*-poly(VAc) (entry 14), (B) aPVA hydrolyzed from the corresponding poly(VAc) homopolymer shown in Fig. 6A, and (C) iPVA hydrolyzed from the corresponding poly(TBVE) macro-CTA.

From ^1H NMR spectra for the resulting polymer after hydrolysis (Fig. 10), the signals of poly(TBVE) in CDCl_3 completely disappeared (Fig. 10B) and all PVA signals in d_6 -DMSO appeared (Fig. 10A). Some tiny peaks around 5.4–6.0 ppm are observed due to the side reactions in living cationic polymerization. In addition, from the analysis of the peak of hydroxyl group of PVA, the percentages of meso and racemo are 50.2 and 49.8, respectively, and for triad tacticity, the percentages of isotactics (I), heterotactics (H) and syndiotactics (S) are 25.7, 48.9, 25.4, respectively. The resulting dyad tacticity is in good agreement with that calculated, m: 50.6 and r: 49.4, which are estimated from

the precursor composition (TBVE₄₈-*b*-VAc₂₀₆) and the dyad tacticity for each segment as shown in Fig. 8. The increase in the meso or isotacticity is due to the isotactic rich of poly(TBVE) segment has changed to PVA by acid hydrolysis.

Fig. 10. ¹H NMR spectra of iPVA-*b*-aPVA (a) in *d*₆-DMSO and (b) in CDCl₃.

The thermal properties of obtained stereoblock PVA, i.e. iPVA-*b*-aPVA were then investigated. Ohgi et. al. summarized the DSC and TGA measurement of high isotactic PVA (HI-PVA, melting point: over 240 °C), low isotactic PVA (LI-PVA, ca.180-230 °C), atactic PVA (A-PVA, ca. 230 °C) and syndiotactic PVA (S-PVA, over 240 °C) [41]. HI-PVA shows high melting temperature and melting curve relatively closed to the

S-PVA as compared to those of the LI-PVA and A-PVA. Furthermore, the melting endothermic curve of LI-PVA is broader and difficult to determine the heat of melting. The different melting points are likely to be due to the different hydrogen bondings. In addition, the high thermal stability of HI-PVA can be seen in term of weight loss because thermal decomposition of LI-PVA occurred easily. DSC measurement of iPVA-*b*-aPVA is shown in Fig. 11. From the thermogram, the glass transition temperature (T_g) shows at 69.5 °C. The T_g is unique in PVA, which is not significantly influenced by the difference in stereoregularity. Interestingly, there are two melting points for PVA at 198.1 °C (T_{m1}) and 237.9 °C (T_{m2}). These values are close to the corresponding melting points for the homopolymers from poly(VAc) and poly(TBVE), which are 215.0 °C and 234.2 °C, respectively (see Fig S3 in Supporting information). Since the product iPVA-*b*-aPVA is block copolymer and has imperfect stereoregularity, both T_{ms} are likely to be shifted toward lower temperatures. This thermal property of the resulting PVA stereoblock copolymer is similar to the result on that of isotactic-atactic stereoblock polyolefines prepared by coordination polymerization [42]. Hence, it can be suggested that obtained PVA has two different geometries which first synthesized by the combination of living cationic vinyl polymerization and RAFT/MADIX polymerization.

Fig. 11. DSC thermogram of PVA stereoblock copolymer (iPVA-*b*-aPVA).

4. Conclusion

In conclusion, novel stereoblock copolymer, iPVA-*b*-aPVA, was successfully synthesized by the transformation of living cationic polymerization of vinyl ethers into RAFT/MADIX polymerization. For living cationic polymerization of IBVE and TBVE, the polymerizations were proceeded under Xanthate 1-HCl adduct/SnCl₄ and Xanthate 1 or 2-CF₃COOH adduct/EtAlCl₂ initiating system in the presence of ethyl acetate. Both systems show living polymerization nature and the resulting polymers had high number average α -end functionality. However, Xanthate 1 is less efficient for the following RAFT/MADIX polymerization of VAc due to the stabilized benzyl radical derived from Xanthate 1 by resonance. The following RAFT/MADIX polymerization of VAc using AIBN at 60 °C was conducted mainly using poly(TBVE) macro-CTA. The poly(TBVE) macro-CTAs synthesized from the Xanthate 2 was able to polymerize VAc smoothly via RAFT/MADIX polymerization, to prepare well-defined diblock copolymer,

poly(TBVE)-*b*-poly(VAc). The resulting block copolymer was then hydrolyzed using KOH in methanol and followed by acid hydrolysis using HBr gas bubbling. The resulting polymer was isotactic rich PVA-*b*-atactic PVA (iPVA-*b*-aPVA), determined by ¹H NMR spectroscopy. From the DSC measurement, the iPVA-*b*-aPVA has one glass transition at 69.5 °C and two melting points according to iPVA and aPVA at 237.9 and 198.1 °C, respectively. This indicates that the obtained PVA has two different geometries, which was first synthesized by the combination of living cationic vinyl polymerization and RAFT/MADIX polymerization.

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