Living Cationic Polymerization of a Novel Bicyclic Conjugated Diene Monomer, Tetrahydroindene, and Its Block Copolymers with Vinyl Ether

Naomi Mizuno,[†] Kotaro Satoh,[†] Masami Kamigaito,*[,†] and Yoshio Okamoto[‡]

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan; and EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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ABSTRACT: The living cationic polymerization of a novel bicyclic conjugated diene monomer, tetrahydroindene (THI) (bicyclo[4.3.0]-2,9-nonadiene), was achieved using the $SnCl_4$-based initiating system, in which the Lewis acid works as an activator for the dormant C−Cl terminal originating from the hydrogen chloride adduct of the 2-chloroethyl vinyl ether as an initiator (**1**) in the presence of a nucleophilic additive such as ethyl acetate. The number-average molecular weights of the obtained polymers increased in direct proportion to the monomer conversion, and the MWDs were narrow throughout the reactions ($M_w/M_n \sim 1.2$). The well-defined terminal structure of the obtained poly(THI) was confirmed by the ^1H NMR and MALDI-TOF MS analysis, which shows the presence of the initiator moiety at the α end and the chlorine at the ω end. The living cationic block copolymerization of isobutyl vinyl ether (IBVE) followed by THI led to the di- and triblock copolymers consisting of the hard nonpolar THI and soft polar IBVE segments for possible application of the triblock copolymer as a thermoplastic elastomer.

Introduction

A bicyclic conjugated diene, tetrahydroindene (THI) (bicyclo-[4.3.0]-2,9-nonadiene), was first synthesized in 1980 though the formation was reported in 1963.[1] This diene can be readily prepared by the Diels−Alder reaction between cyclopentadiene and butadiene, leading to the nonconjugated counterpart (bicyclo[4.3.0]-3.7-nonadiene)[2] and the following isomerization of the Diels−Alder product catalyzed by $Cp_2TiCl_2/LiAlH_4$.[3] This bicyclic compound has recently been employed as a novel diene monomer for vinyl addition polymerization and showed a high reactivity during cationic polymerization to produce polymers with new rigid hydrocarbon backbones consisting of bicyclic structures of five- and six-membered rings.[4,5] This kind of alicyclic polymers, in general, and/or its hydrogenated product, thus have unique physical and chemical properties, particularly good mechanical, electrical, and optical characteristics, as well as a superior weathering and heat-resistant behavior.[6] The development of the living or controlled cationic polymerization of this monomer would thus expand the possibilities of this new alicyclic hydrocarbon polymer for further functional materials.

Living or controlled cationic polymerization was first discovered for vinyl ether and isobutylene[7] and is now applicable to a variety of monomers, including styrene, styrene derivatives,[8−10] indene,[11,12] cyclopentadiene,[13] β-pinene,[14] norbornadiene,[15] etc., by the designed initiating systems consisting of the appropriate combination of an initiator (protogen or cationogen) and a Lewis acid (catalyst) depending on the monomers. A key to the living cationic polymerization is the stabilization of the unstable carbocations via the nucleophilic interaction of the counteranion originating from the initiator and the catalyst as well as the Lewis-acid-mediated fast reversible interconversion of the carbocationic species into the dormant species with the covalent carbon−halogen or ester bonds. In general, hydrogen iodide, chloride, and acetic acid or its adduct with the monomer are employed as the initiators, while metal chlorides, bromides, or alkoxides are employed as Lewis acid catalysts. Among them, the tin tetrachloride ($SnCl_4$)-based initiating system has been used for a wide range of monomers such as vinyl ethers,[16,17] styrenes,[8−10] and cyclopentadiene,[13] sometimes in the presence of added bases or added common ion salts if necessary.

This paper reports the first example of the living cationic polymerization of THI with an initiating system consisting of the HCl adduct of 2-chloroethyl vinyl ether (CEVE) and $SnCl_4$ (Scheme 1) and the block copolymerization of a vinyl ether (VE). The latter part will lead to a novel thermoplastic elastomer that consists of a hard and nonpolar poly(THI) segment with high service temperatures, whereas the poly(VE) serves as a soft and polar segment. A similar approach to the thermoplastic elastomer based on the living cationic block polymerization was reported for a combination of isobutylene as the soft segment monomer and a cyclic monomer,[18] such as indene,[19] acenaphthylene,[20] and norbornadiene,[15] as the hard segment.

Experimental Section

Materials. Bicyclo[4.3.0]-2,9-nonadiene (THI) was kindly provided from Nippon Oil Corporation and used after distillation from calcium hydride under reduced pressure (42 °C/8.5 mmHg). Isobutyl vinyl ether (IBVE) (Tokyo Kasei, >99%), 2-chloroethyl vinyl ether (CEVE) (Tokyo Kasei, >97%), and 1,4-cyclohexanedimethanol divinyl ether (CHDMVE) (Aldrich, >98%) were washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled from calcium hydride before use. Toluene (Wako, >97%) as a solvent and 1,2,3,4-tetrahydronaphthalene (Kishida, >99.5%) as an internal standard for gas chromatography were dried overnight over calcium chloride and distilled from sodium benzophenone ketyl before use. Diethyl ether (Et_2O) and ethyl acetate (EtOAc) were used and were dried

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* To whom correspondence should be addressed. E-mail: kamigait@apchem.nagoya-u.c.jp.

[†] Nagoya University, Department of Applied Chemistry.

[‡] Nagoya University, EcoTopia Science Institute.

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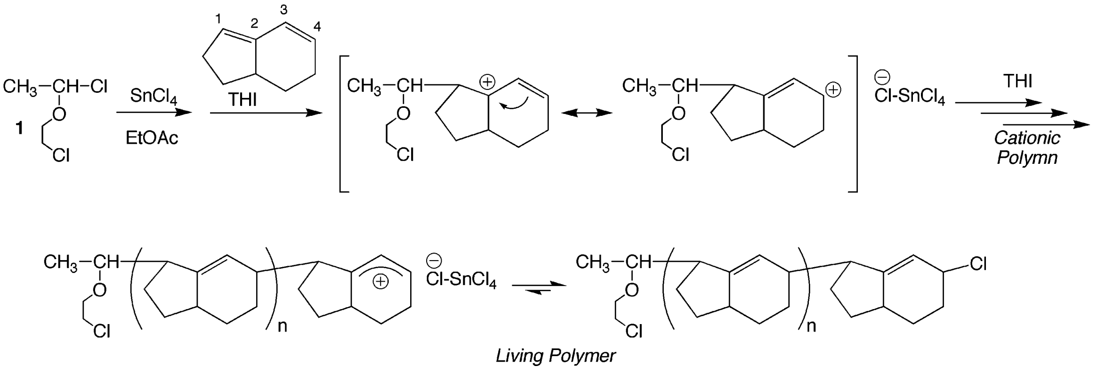
Scheme 1



overnight over calcium chloride and distilled from calcium hydride before use. $SnCl_4$ (Aldrich, 99.995%) was used as received. The CEVE−HCl adduct (**1**) and the difunctional initiator (CHDMVE−2HCl, **2**) were prepared by bubbling dry HCl gas into 1.0 M solution of the corresponding monomer at −78 or 0 °C, and then dry nitrogen was bubbled to remove excess HCl, as reported.[21]

Polymerization. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is given below. The reaction was initiated by sequential addition of prechilled solutions of **1** (0.015 mmol; 0.3 mL of 50.0 mM in toluene) and mixture solutions (0.6 mL) of $SnCl_4$ (0.03 mmol) and EtOAc (0.075 mmol) via dry syringes into a monomer solution (in toluene, 2.1 mL) containing THI (1.5 mmol) and 1,2,3,4-tetrahydronaphthalene (0.1 mL). The total volume of the reaction mixture was 3.0 mL. After stirring at −78 °C, the polymerization was terminated with prechilled methanol (1.0 mL) containing a small amount of ammonia. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with 1,2,3,4-tetrahydronaphthalene as an internal standard. The polymer yield by gravimetry was in good agreement with the gas chromatographic conversion of the monomer.

The quenched reaction mixture was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers.

Measurements. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography [Shimadzu GC-8A equipped with a thermal conductivity detector and a 3.0 mm i.d. × 2 m stainless steel column packed with SBS-200 (Shinwa Chemical Industries Ltd.) supported on Shimalite W; injection and detector temperature = 200 °C, column temperature = 160 °C] with 1,2,3,4-tetrahydronaphthalene as an internal standard under He gas flow. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Gemini 2000 spectrometer operating at 400 MHz. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the product (co)polymers were determined by size-exclusion chromatography (SEC) in THF at 40 °C on two polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-980 precision pump and a Jasco 930-RI detector. The columns were calibrated against eight standard polystyrene samples (Shodex; M_p = 520−900 000; M_w/M_n = 1.01−1.14). The MALLS analysis was performed in THF on a Dawn DSP instrument (Wyatt Technology; Ga−As laser, λ = 690 nm). The refractive index increments (dn/dc) were measured in THF at 40 °C on an Optilab rEX (Wyatt Technology) (λ = 690 nm). MALDI-TOF MS spectra were measured on an Applied Biosystems Voyager-DE STR spectrometer (reflector mode) with dithranol (1,8,9-anthracenetriol) as the ionizing matrix and silver trifluoroacetate as the ion source. The experiment was carried out at an accelerating potential of 22 kV, where 256 laser shots were accumulated. Dynamic tensile storage (E') and loss (E'') moduli and tan δ (= E''/E') were measured on a UBM Rheogel-E4000 spectrometer, operating at 11 Hz frequency; heating rate: 10 °C/min. Transmission electron microscope (TEM) observations were carried out on a transmission electron microscope H-7100 FA (Hitachi, Ltd.), operated at 100 kV. Thin films were exposed to OsO_4 vapor for a few hours to stain the poly(THI) block.

Results and Discussion

1. Living Cationic Polymerization of THI. *(a) Polymerization of THI with 1/SnCl₄.* We herein employed $SnCl_4$ as an activator for the polymerization of THI, in which the hydrogen chloride adduct of the 2-chloroethyl vinyl ether (**1**) was employed as an initiator. The cationic polymerization of THI was first carried out in toluene at −78 °C with $SnCl_4$ in the presence or absence of **1** ($[\mathbf{1}]_0$ = 5.0 mM, $[SnCl_4]_0$ = 5.0 mM; Figure 1).

Under these conditions, the polymerization was almost instantaneous and resulted in polymers with uncontrolled molecular weights and broad molecular weight distributions (MWDs). However, upon the addition of a Lewis base, such as diethyl ether (Et_2O) or ethyl acetate (EtOAc), the polymerization with **1**/$SnCl_4$ was clearly retarded to give the polymers with relatively narrow MWDs ($M_w/M_n \sim 1.2$), similar to the polymerization of cyclopentadiene.[13] The number-average molecular weights (M_n) of the obtained polymers were directly proportional to the monomer conversion while lower than the calculated values on the assumption that one molecule of **1** generates one polymer chain. This is because the molecular weights were obtained by size exclusion chromatography (SEC) on the basis of a polystyrene calibration (see the Experimental

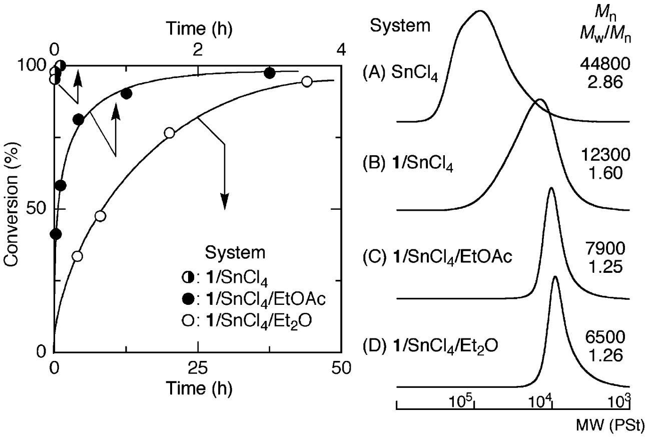


Figure 1. Polymerization of tetrahydroindene (THI) with **1**/Lewis acid initiating systems in toluene at −78 °C: $[THI]_0$ = 0.5 M; $[\mathbf{1}]_0$ = 5.0 mM; $[\mathbf{1}]_0$ = 5.0 mM; [Lewis acid]$_0$ = 5.0 mM (without additives) or 10.0 mM (with additives); $[EtOAc]_0$ = 25.0 mM; $[Et_2O]_0$ = 100 mM. Systems: (◑) **1**/$SnCl_4$; (●) **1**/$SnCl_4$/EtOAc; (○) **1**/$SnCl_4$/Et_2O. The size-exclusion chromatograms are for the polymers obtained at 62% (for A) and ca. 95% (for B, C, and D) conversion.

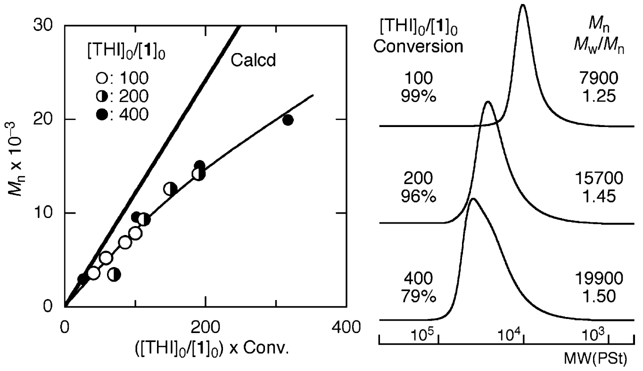


Figure 2. M_n curves and size-exclusion chromatograms of poly(tetrahydroindene) obtained with varying the [THI]$_0$/[**1**]$_0$ ratio in toluene at −78 °C; [THI]$_0$/[**1**]$_0$ = 100 (○), 200 (◑), or 400 (●; [THI]$_0$ = 0.50 (for ○ and ◑) or 1.0 M (for ●); [SnCl$_4$]$_0$ = 10.0 mM; [EtOAc]$_0$ = 25.0 mM. The diagonal bold line indicates the calculated M_n, assuming the formation of one living polymer per one **1** molecule against polystyrene standards.

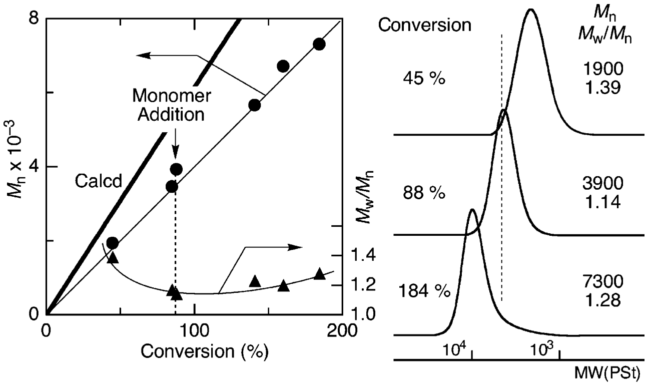


Figure 3. M_n curves and size-exclusion chromatograms of poly(tetrahydroindene) obtained in a monomer-addition experiment in the polymerization with **1**/SnCl$_4$ in the presence of EtOAc in toluene at −78 °C: [THI]$_0$ = [THI]$_{add}$ = 0.25 M; [**1**]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 10.0 mM; [EtOAc]$_0$ = 25.0 mM. The diagonal bold line indicates the calculated M_n, assuming the formation of one living polymer per one **1** molecule against polystyrene standards.

Section),[22] and this point will be discussed later. Thus, the initiating system consisting of **1** and SnCl$_4$ yielded well-controlled polymers in the presence of the added bases, which interact with the carbocationic propagating species and/or the Lewis acid. The appropriate amount of the added bases for the living polymerization depended on their basicity, i.e., the less basic the additive is, the more its amount should be ([Et$_2$O]$_0$ = 100 mM and [EtOAc]$_0$ = 25 mM, respectively), similar to the other living cationic polymerizations.[13,23,24]

A series of further experiments were done by varying the [THI]$_0$/[**1**]$_0$ ratio from 50 to 400, while the [SnCl$_4$]$_0$ and [EtOAc]$_0$ remained constant. The polymerizations were almost quantitative under all the conditions, and the rate increased with the increasing [**1**]$_0$. Figure 2 shows the M_n values and SEC curves of the polymers obtained with **1**/SnCl$_4$ in toluene at different [THI]$_0$/[**1**]$_0$ ratios with various conversions, where [THI]$_{consumed}$/[**1**]$_0$ = ([THI]$_0$/[**1**]$_0$) × conversion. The M_n was inversely proportional to [**1**]$_0$, although the MWD became somewhat broader as the [THI]$_0$/[**1**]$_0$ ratio increased (M_w/M_n ~ 1.6 at [THI]$_0$/[**1**]$_0$ = 400). This is probably due to the unignorable initiation from the adventitious water and/or the small amount of chain transfer during the polymerization at such a low concentration of the initiator ([**1**]$_0$). These results also indicated that the polymerization of THI proceeded in a living and/or controlled fashion and that all of the polymer chains were most probably generated from **1** to give polymers with the predetermined M_n values by the [THI]$_0$/[**1**]$_0$ ratio.

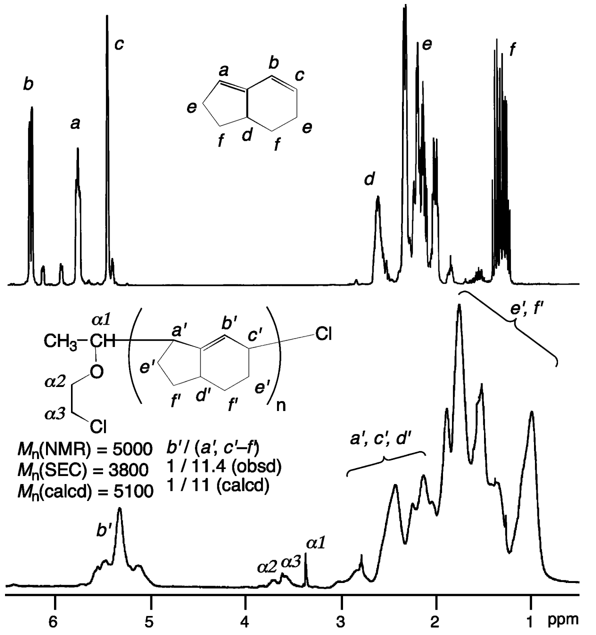


Figure 4. ^{1}H NMR spectrum (CDCl$_3$, 25 °C) of poly(tetrahydroindene) (M_n = 3800, M_w/M_n = 1.29) obtained in the polymerization with **1**/SnCl$_4$/EtOAc in toluene at −78 °C; [THI]$_0$ = 0.50 M; [**1**]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 10.0 mM; [EtOAc]$_0$ = 25.0 mM; monomer conversion = 40%.

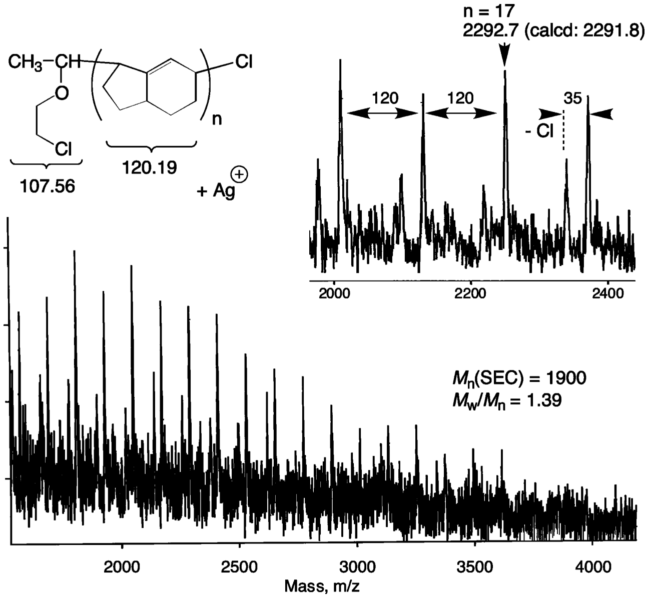


Figure 5. MALDI-TOF-MS spectrum of poly(tetrahydroindene) (M_n = 1900, M_w/M_n = 1.39) obtained in the same experiments as for Figure 3; monomer conversion = 45%.

(b) Monomer Addition Experiment. To examine the living nature of the THI polymerization with **1**/SnCl$_4$/EtOAc at −78 °C, a fresh feed of THI was added to the reaction mixture just before the initial charge of the monomer had almost been completely consumed (conversion ~90%). The added THI was smoothly polymerized at nearly the same rate as during the first stage. Figure 2 shows the M_n, M_w/M_n, and SEC curves of the polymers. Even after the monomer addition, the molecular weights continuously increased in direct proportion to the monomer conversion. The peak of the SEC curves shifted to the higher molecular weight region as the polymerization proceeded, whereas the MWDs slightly broadened after the

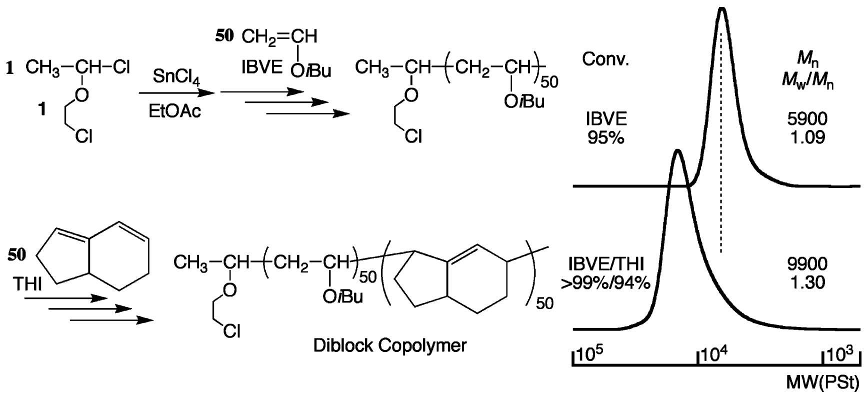


Figure 6. Size-exclusion chromatograms of poly(IBVE) and IBVE−THI diblock copolymers obtained with **1**/$SnCl_4$/EtOAc in toluene at −78 °C: $[IBVE]_0 = [THI]_{add} = 0.25$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[SnCl_4]_0 = 10.0$ mM; $[EtOAc]_0 = 25.0$ mM. Conversions are over 90% for both monomers.

addition. Thus, it was demonstrated that the HCl−vinyl ether adduct leads to the living cationic polymerization of THI in conjunction with $SnCl_4$ as a Lewis acid activator in the presence of EtOAc.

(c) Polymer Analysis. The structure of the polymers obtained with **1** and $SnCl_4$ in the presence of EtOAc in toluene was analyzed by ^{1}H NMR spectroscopy. Figure 4 shows the ^{1}H NMR spectra of the monomer and typical sample obtained with **1**/$SnCl_4$/EtOAc after quenching the polymerization with methanol at 41% conversion [M_n (SEC) = 3800]. The spectrum shows the characteristic signals of poly(THI), i.e., the unsaturated olefinic (b') and saturated aliphatic protons (a', c', d', e', and f').[3] The relative peak area ratio of the aliphatic to the olefinic protons [$(a' + c' + d' + e' + f')/b'$] was 11.4, which agreed with the calculated value, 11, assuming that the polymerization proceeded via the 1,4-addition. Among the several possible pathways for the propagation, the 1,4-enchaiment is the most favorable in terms of the formation of the conjugated tertiary and secondary carbocations via addition to the 1-position of the monomer and the relatively small steric hindrance upon propagation from the 4-position (see Scheme 1).[5] The 1,2-enchainment may happen but leads to a higher olefinic proton content, $(a' + c' + d' + e' + f')/b' = 10/2$.

In addition to these large absorptions, small signals due to the end groups appeared (3.3−3.8 ppm). They are attributed to the methine (α1) and methylene (α2 and α3) protons adjacent to the oxygen or the chlorine at the α end derived from the HCl adduct of CEVE (**1**) as an initiator. The molecular weight determined from the relative peak area of the main-chain repeat units (b') to the initiator moiety (α1−α3) [M_n (NMR) = 5000] was higher than that based on the SEC [M_n (SEC) = 3800], but agreed well with the calculated value [M_n (calcd) = 5100]. We also found that the absolute molecular weight of poly(THI) obtained by multiangle laser light scattering (MALLS) is higher than that based on the polystyrene standard calibration due to the difference in their hydrodynamic volumes.[22] Thus, one molecule of **1** generates one living polymer chain to give polymers with controlled molecular weights.

The poly(THI) obtained by the living cationic polymerization with **1**/$SnCl_4$ was also analyzed by matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF MS) in the presence of dithranol as the matrix and CF_3CO_2Ag as the ionizing agent (Figure 5). The spectrum consists of a series of peaks, each separated by a 120.2 Da interval, which corresponds to the molecular weight of the THI monomer. The molecular weight of each individual peak was very close to the calculated value for $[CH_3{-}CH(OCH_2CH_2Cl){-}(THI)_n{-}Cl/Ag^+]$, i.e., poly(THI) processing one initiator moiety at the α end, one chlorine atom at the ω end, and the silver ion from the salt for the MS analysis. This again indicates that the **1**/$SnCl_4$ initiating system produces the poly(THI) with well-defined terminal groups. This also shows that the Cl-capped poly(THI) are relatively stable toward the laser ionization, compared to the fact that similar Cl-capped polymers synthesized via living cationic or transition-metal-catalyzed living radical polymerization often lose the halogen at the ω end during the MS analysis.[25,26] However, a minor series of peaks with a 35 Da lower mass was observed, which suggests some laser-induced halogen loss during the MS analysis.

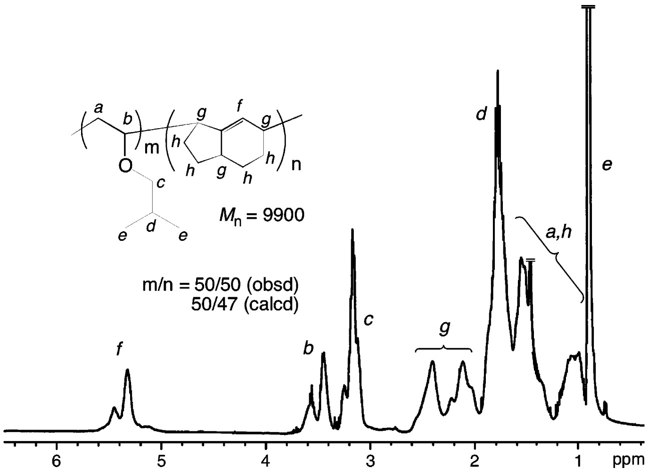


Figure 7. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of IBVE-THI block copolymer ($M_n = 9900$, $M_w/M_n = 1.30$) obtained with **1**/$SnCl_4$/EtOAc in toluene at −78 °C.

2. Block Copolymerization with Vinyl Ether. *(a) Diblock Copolymerization.* The success of the living or controlled cationic polymerization of THI thus led to block copolymerizations with isobutyl vinyl ether (IBVE), one of the most commonly used monomers for living cationic polymerizations, which can afford rubbery polymers with soft segments. The sequential block copolymerization of THI and IBVE was then investigated using the **1**/$SnCl_4$-based initiating system. IBVE was first polymerized with **1**/$SnCl_4$ in the presence of EtOAc in toluene at −78 °C to produce the living poly(IBVE) with fairly narrow MWDs ($M_w/M_n < 1.1$). After a nearly complete consumption of IBVE, a feed of THI, equimolar to the vinyl ether monomer, was added to the living poly(IBVE) solution. The second monomer was also smoothly polymerized. As shown in Figure 6, the MWD curves shifted to higher molecular weights upon the THI addition, although the MWDs became somewhat broadened. Thus, the **1**/$SnCl_4$/EtOAc system

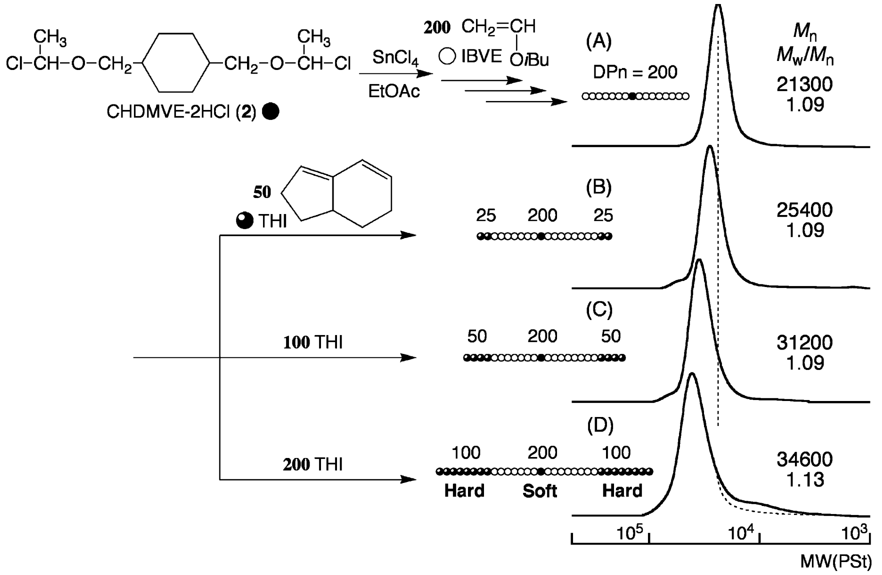


Figure 8. Size-exclusion chromatograms of poly(IBVE) (A) and THI−IBVE−THI triblock copolymers (B, C, and D) obtained with a difunctional initiator (**2**)/$SnCl_4$/EtOAc in toluene at −78 °C: $[IBVE]_0 = 1.0$ M; $[THI]_{add} = 0.25$ (B), 0.50 (C), or 1.0 M (D); $[\mathbf{2}]_0 = 5.0$ mM; $[SnCl_4]_0 = 10.0$ mM; $[EtOAc]_0 = 25.0$ mM. Conversions are over 90% for both monomers.

was also effective for the block copolymerization of IBVE and THI.

Figure 7 shows the ^{1}H NMR spectrum of the obtained block copolymer. The block copolymers also gave characteristic signals of the main-chain units of THI and those of IBVE. The unit ratio of THI to IBVE was calculated from the peak intensity ratio of the olefinic protons (a) in the THI unit to the methine and methylene protons (d and e) adjacent to the oxygen atom in the IBVE unit. The observed ratio, 50/50 (THI/IBVE), was in good agreement with the calculated value (47/50) from the monomer feed ratio and the gas chromatographic conversions. Along with the peak shift in the SEC curves, this NMR analysis indicates the formation of the block copolymers of IBVE and THI though successful cross propagation from the growing poly(IBVE) terminal to THI.

(b) ABA Triblock Copolymer. Furthermore, the synthesis of the THI-*b*-IBVE-*b*-THI triblock copolymers was investigated using a bifunctional initiator (**2**) prepared from a divinyl ether and hydrogen chloride.[7,27] The block copolymerization of IBVE followed by THI was carried out using the **2**/$SnCl_4$ initiating system in the presence of EtOAc by varying the feed ratio of THI to IBVE. The polymerization of IBVE and the following THI smoothly proceeded under all the conditions to provide an almost quantitative conversion.

Figure 8 shows the SEC curves of the poly(IBVE) and the triblock copolymers obtained with the bifunctional initiator for a series of different feed ratios of THI. All the polymers had relatively narrow MWDs, indicating the formation of the triblock copolymers, which were also suggested by the ^{1}H NMR analysis. These copolymers can be expected as novel thermoplastic elastomers that consist of hard and nonpolar THI segments and the soft and polar VE segments along with the relatively high service temperature of poly(THI).

The dynamic mechanical property of the THI−IBVE−THI triblock copolymer was evaluated by the dynamic viscoelasticity. Figure 9 shows the dynamic tensile storage (E') and loss (E'') moduli and tan δ ($= E''/E'$) as a function of the temperature for a typical sample of the THI−IBVE−THI triblock copolymer; the polymerization degrees of each segment determined by the initial feed ratio and ^{1}H NMR spectroscopy were 50−200−50 for THI−IBVE−THI, respectively. The copolymer exhibited the dynamic mechanical spectrum of a thermoplastic elastomer, i.e., two loss peaks in the modulus associated with the glass-transition temperature of the rubbery poly(IBVE) midblock and that of the hard poly(THI) outer blocks. This indicates that the phase separations between the two segments took place and the copolymer could act as an elastomer between the two transition temperatures (ca. 10−170 °C).

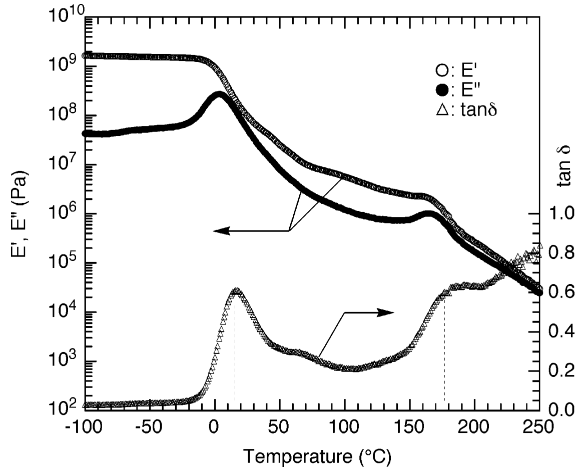


Figure 9. Dynamic tensile storage (E') and loss (E'') moduli and tan δ ($= E''/E'$) as a fraction of temperature for a THI−IBVE−THI triblock copolymer ($M_n = 30\,100$, $M_w/M_n = 1.19$) obtained with a difunctional initiator (**2**)/$SnCl_4$/EtOAc in toluene at −78 °C: $[IBVE]_0 = 1.0$ M; $[THI]_{add} = 0.50$ M; $[\mathbf{2}]_0 = 5.0$ mM; $[SnCl_4]_0 = 10.0$ mM; $[EtOAc]_0 = 25.0$ mM. Heating rate: 10 °C/min; frequency: 11 Hz.

The morphology of the THI−IBVE−THI triblock copolymer was also evaluated by using TEM. The contrast of the domains could be brought out after 8 h of annealing at 80 °C of the sample and a few hours of staining of thin films by OsO_4 vapor, where the THI segments with unsaturated double bonds appear dark. The TEM images of the copolymer showed a typical microphase separated structure in the expected alternating lamellar morphology (Figure 10). Thus, the copolymerizations of THI and vinyl ethers will lead to novel thermoplastic elastomers that consist of a nonpolar hard segment and polar soft segments with wide-ranging service temperatures due to the high T_g of poly(THI).

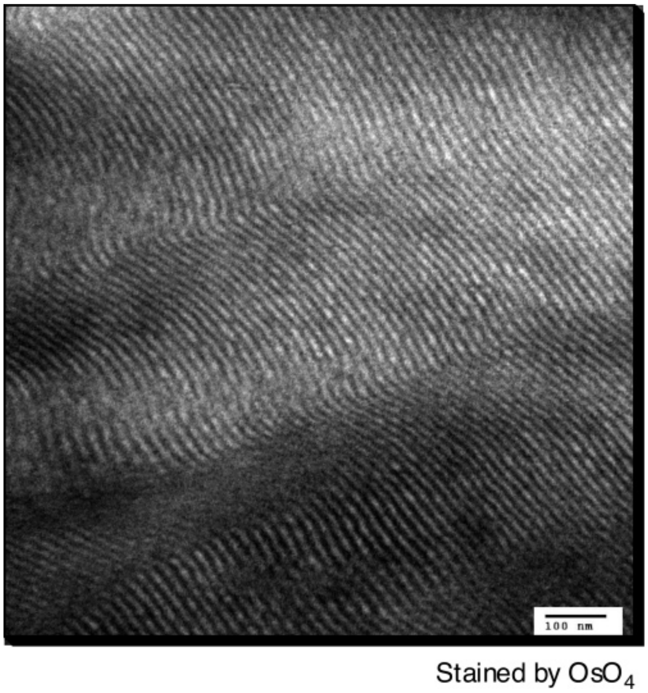


Figure 10. Transmission electron microscope (TEM) image of a THI−IBVE−THI triblock copolymer (M_n = 30 100, M_w/M_n = 1.19) obtained with a difunctional initiator (**2**)/SnCl$_4$/EtOAc in toluene at −78 °C: $[\text{IBVE}]_0$ = 1.0 M; $[\text{THI}]_{\text{add}}$ = 0.50 M; $[\mathbf{2}]_0$ = 5.0 mM; $[\text{SnCl}_4]_0$ = 10.0 mM; $[\text{EtOAc}]_0$ = 25.0 mM. Stained by OsO$_4$.

Conclusion

In conclusion, the living cationic polymerization of THI was first demonstrated by the **1**/SnCl$_4$ initiating systems in the presence of EtOAc at −78 °C to afford polymers with controlled molecular weights, narrow MWDs, and well-defined chain end groups. This system was also effective for the block copolymerization with vinyl ether.

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