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Living Cationic Polymerization of Styrene with TiCl$_3$(O*i*Pr) as a Lewis Acid Activator[1]

Toshiyuki Hasebe, Masami Kamigaito, and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

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ABSTRACT: Living cationic polymerization of styrene has been achieved with TiCl$_3$(O*i*Pr) as an activator, where its Lewis acidity was modulated by introduction of an electron-donating isopropoxy group onto highly electron-deficient titanium(IV) chloride, in conjunction with HCl−styrene adduct (**1**) and *n*Bu$_4$NCl in CH$_2$Cl$_2$ at −40 and −78 °C. The number-average molecular weights (M_n) of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values, assuming that one polymer chain is generated per molecule of adduct **1**. The molecular weight distributions were narrow throughout the reactions ($\bar{M}_w/\bar{M}_n \sim 1.1$). In contrast, a stronger Lewis acid, TiCl$_4$, induced ill-controlled polymerizations, and a weaker titanium(IV) acid, TiCl$_2$(O*i*Pr)$_2$, was not effective in the styrene polymerizations. Thus, the selection of Lewis acids is crucial for the living cationic polymerizations so that their Lewis acidity is fit for the monomer reactivity.

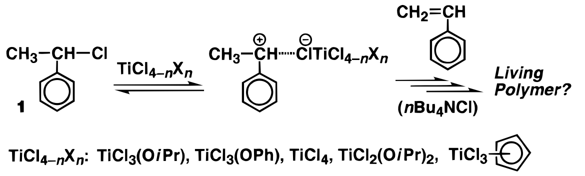
Introduction

Styrene is a commercially available vinyl monomer that undergoes polymerizations via cationic as well as radical, anionic, and coordination pathways. In cationic polymerizations, its lack of strongly electron-donating groups renders the growing carbocation unstable, and it thereby suffers from side reactions such as chain transfer accompanied by β-proton elimination and Friedel−Crafts alkylation on the phenyl ring of the monomer unit. Thus, control of the cationic polymerization of styrene has been considered difficult, in contrast to its well-established living anionic counterpart.[2]

Such a view on the living cationic polymerization of styrene, however, has been changing, in accordance with the developments of living processes for other vinyl monomers with electron-donating substituents like vinyl ethers.[2,3] We have found, for example, that the SnCl$_4$-based initiating systems induce living and better-controlled cationic polymerizations in terms of polymer molecular weight and molecular weight distribution (MWD).[4,5] The initiating system of choice consists of the HCl adduct of styrene [**1**, 1-phenylethyl chloride, CH$_3$CH(Ph)Cl] as an initiator, and in the presence of tetra-*n*-butylammonium chloride (*n*Bu$_4$N$^+$Cl$^-$) it affords polystyrenes with narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.1$) and molecular weights controlled by the monomer/initiator mole ratio. The success is probably attributed to the use of the suitable Lewis acid for the monomer reactivity and also the added salt that may stabilize the unstable carbocation, although its actual role is now under discussion.[6,7] More recently, it has been reported that TiCl$_4$-based initiating systems gave the polymers with controlled molecular weights in the presence of a nitrogen base, including *N*,*N*-dimethylacetamide and sterically hindered pyridines.[8−11] However, the MWDs with the TiCl$_4$-based initiating systems were broader ($\bar{M}_w/\bar{M}_n \sim 1.8$) than those with the SnCl$_4$-based counterparts. Another possibility for living styrene polymerization was reported, where the adduct of acetic acid and *p*-methylstyrene was coupled with BCl$_3$ to give polymers with controlled molecular weights but rather broad MWDs ($\bar{M}_w/\bar{M}_n \sim 5−6$).[12]

In contrast to such a relative paucity of living or controlled cationic systems for styrene polymerizations, a wide variety of living processes are now available for vinyl ethers and isobutene.[3] It has been revealed that one of the keys to the living or controlled cationic polymerizations is the selection of Lewis acids suited for the monomer reactivity. For example, we have recently reported that living cationic polymerization of vinyl ethers can be achieved with the use of substituted titanium(IV) chlorides, such as TiCl$_2$(O*i*Pr)$_2$, where their Lewis acidity is modulated by electron-donating alkoxy groups introduced onto the metal, so as to be suited for the cationic reactivity of the monomers.[13] Similar modulation of TiCl$_4$-based Lewis acids was investigated in the living polymerizations of *p*-methylstyrene[14a] and α-methylstyrene[14b] by in-situ mixing of TiCl$_4$ and Ti(OR)$_4$. Also, TiCl$_3$(O*n*Bu) was employed for indene.[15] Such modulation of the Lewis acidity of metal halides with substituents is a more direct method than the addition of nucleophilic compounds,[2,4,5] which is also effective in weakening strong Lewis acids for the control of cationic polymerizations.

In this study, we have examined living cationic polymerization of styrene with titanium(IV)-based Lewis acids (TiCl$_{4-n}$X$_n$) modified by the number and nature of the substituents (X = O*i*Pr, OPh, Cp) in conjunction with **1** as an initiator (eq 1). As with vinyl ethers,[13] these compounds were separately prepared and isolated and thus well-defined in structure and purity.



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Results and Discussion

Living Cationic Polymerization with TiCl$_3$(O*i*Pr). Our previous studies showed that TiCl$_2$(O*i*Pr)$_2$, a titanium(IV) chloride disubstituted with electron-donating isopropoxy groups, is effective in inducing living polymerization of isobutyl vinyl ether.[13] On the basis of the results, we herein employed its monosubstituted analog, TiCl$_3$(O*i*Pr), a stronger Lewis acid than the disubsti-

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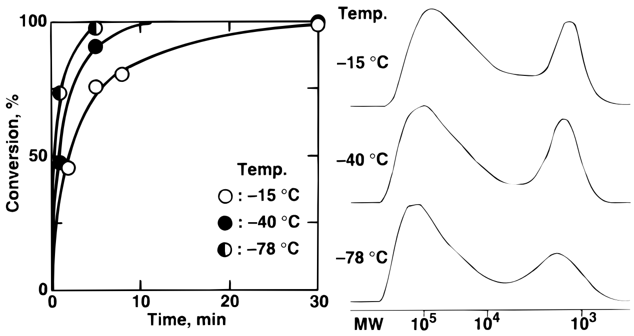

Figure 1. Polymerization of styrene with **1**/TiCl$_3$(O*i*Pr) in CH$_2$Cl$_2$ at −78 (◐), −40 (●), and −15 °C (○): [M]$_0$ = 1.0 M; [**1**]$_0$ = 20 mM; [TiCl$_3$(O*i*Pr)]$_0$ = 100 mM.

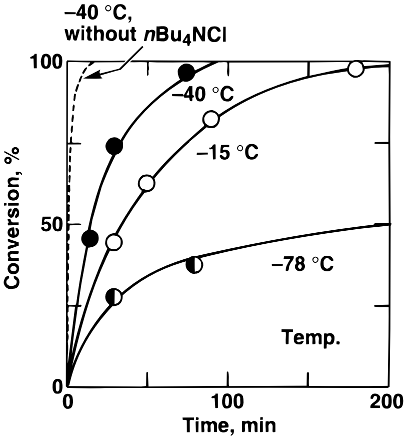

Figure 2. Polymerization of styrene with **1**/TiCl$_3$(O*i*Pr)/*n*Bu$_4$NCl in CH$_2$Cl$_2$ at −78 (◐), −40 (●), and −15 °C (○): [M]$_0$ = 1.0 M; [**1**]$_0$ = 20 mM; [TiCl$_3$(O*i*Pr)]$_0$ = 100 mM; [*n*Bu$_4$NCl]$_0$ = 20 mM.

tuted analog. Thus, styrene polymerization was carried out with a combination of **1** and TiCl$_3$(O*i*Pr) in CH$_2$Cl$_2$ at −78, −40, and −15 °C (Figure 1).

The **1**/TiCl$_3$(O*i*Pr) initiating system induced fast and efficient polymerizations of styrene without an induction phase. The lower the temperature, the faster the reaction. This is probably due to the increase in solvent polarity with lowering temperature and/or the negative activation energy for propagation.[15b]

The MWDs of the polymers were bimodal, irrespective of temperature. The higher polymer fraction had a broad MWD whose peak molecular weight stayed virtually unchanged throughout the reaction, whereas the lower part was of a much narrower MWD that shifted progressively toward higher molecular weight with increasing conversion. These observations were similar to the polymerizations of styrene with **1**/SnCl$_4$ in the absence of *n*Bu$_4$NCl,[5,6] and the higher fraction is of the polymers generated via "dissociated" or free-ion species and the lower via the "nondissociated" or ion-pair species.

Noting the effects of salts such as *n*Bu$_4$NCl on the **1**/SnCl$_4$-mediated systems,[5] which eliminate the higher polymer fraction, we then investigated the polymerizations with **1**/TiCl$_3$(O*i*Pr) in the presence of this additive. Under these conditions, polymerizations were retarded, as shown in Figure 2, the fastest at −40 °C and the slowest at −78 °C. The latter is probably due to the low solubility of the Lewis acid in the presence of *n*Bu$_4$NCl at this low temperature.

Figure 3 shows the $\bar{M}_n$ values and MWDs of the polymers obtained in the presence of *n*Bu$_4$NCl. The added salt converts the bimodal MWD into a monomodal distribution by suppression of the fraction of free-ion species.[5,6] The $\bar{M}_n$ increased in direct proportion to monomer conversion and agreed well with the calculated values, assuming that one polymer chain is formed per molecule of **1**, specifically at −40 and −78 °C. However, the $\bar{M}_n$ values of the polymers obtained at −15 °C were a little smaller than the calculated values, probably due to chain-transfer reaction. The MWDs were narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$) at −15 and −40 °C but slightly broader at −78 °C, which is ascribed to slow interconversion between the dormant and the activated species. These results indicate that the **1**/TiCl$_3$(O*i*Pr) initiating system leads to living cationic polymerization of styrene at temperatures below −40 °C, where the molecular weights and their distributions are well controlled.

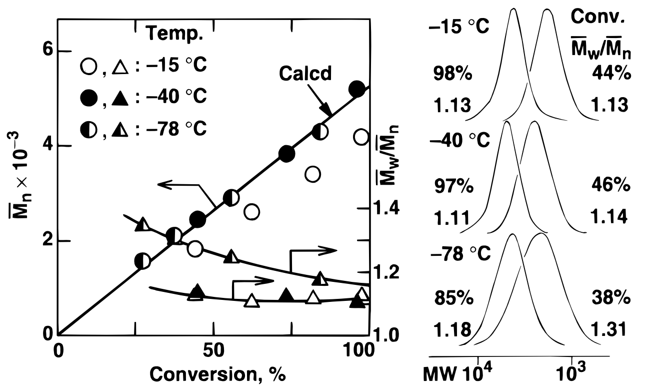

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of polystyrene obtained with **1**/TiCl$_3$(O*i*Pr)/*n*Bu$_4$NCl in CH$_2$Cl$_2$ at −78 (◐,◭), −40 (●,▲), and −15 °C (○,△): [M]$_0$ = 1.0 M; [**1**]$_0$ = 20 mM; [TiCl$_3$(O*i*Pr)]$_0$ = 100 mM; [*n*Bu$_4$NCl]$_0$ = 20 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

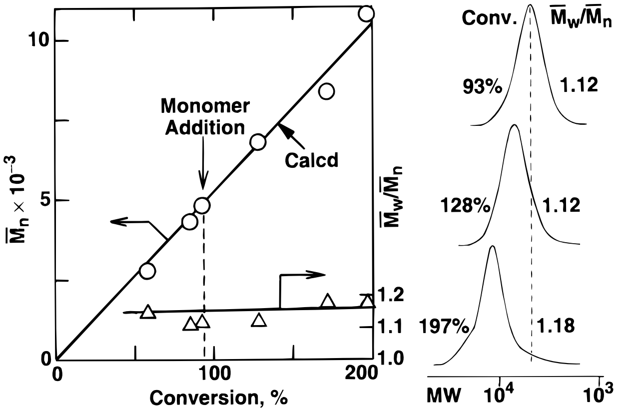

Figure 4. Monomer addition experiments in the polymerization of IBVE with **1**/TiCl$_3$(O*i*Pr)/*n*Bu$_4$NCl in CH$_2$Cl$_2$ at −40 °C: [M]$_0$ = [M]$_{add}$ = 1.0 M; [**1**]$_0$ = 20 mM; [TiCl$_3$(O*i*Pr)]$_0$ = 100 mM; [*n*Bu$_4$NCl]$_0$ = 20 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

To examine the living nature of these polymerizations, a fresh feed of styrene was added to the reaction mixture just before the initial charge of the monomer had been completely polymerized (Figure 4). The added monomer was smoothly polymerized, and the $\bar{M}_n$ values further increased in direct proportion to monomer conversion and agreed well with the calculated values, while the MWDs stayed narrow after the monomer addition ($\bar{M}_w/\bar{M}_n \leq 1.2$). This shows that living cationic polymerization of styrene is possible not only with SnCl$_4$ but

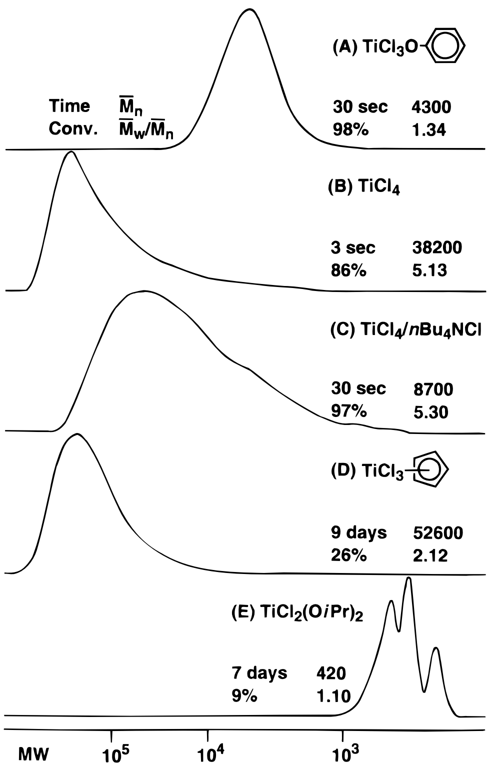

Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of polystyrene obtained with **1**/titanium(IV) compounds in CH_2Cl_2 at −78 (A, B, C), and −15 °C (D, E): (A) $[TiCl_3(OPh)]_0/[nBu_4NCl]_0 = 100/20$ mM; (B) $[TiCl_4]_0 = 10$ mM; (C) $[TiCl_4]_0/[nBu_4NCl]_0 = 30/20$ mM; (D) $[TiCl_3Cp]_0 = 100$ mM; (E) $[TiCl_2(OiPr)_2]_0 = 100$ mM. $[M]_0 = 1.0$ M; $[\mathbf{1}]_0 = 20$ mM.

also with the modified titanium(IV) chloride, $TiCl_3(OiPr)$, where its Lewis acidity is weakened by introducing one isopropoxy group on the titanium center.

The reaction with $TiCl_3(OiPr)$ was much faster than that with $SnCl_4$ under the same conditions; i.e., at −78 °C, 38% conversion in 80 min with $TiCl_3(OiPr)$, versus 37% in 19 h with $SnCl_4$ (see Figure 2). This suggests that the titanium version is a stronger Lewis acid than $SnCl_4$ for styrene polymerizations with 1-phenylethyl chloride.

Polymerizations with Other Titanium(IV) Compounds. When coupled with **1**, other titanium(IV) compounds were also examined for styrene. For example, $TiCl_3(OPh)$ led to faster polymerizations even at −78 °C, where the conversion reached 100% within 2 min. This is due to the stronger Lewis acidity of the monophenoxy compound, because the phenoxy group is less electron-donating than isopropoxy. Such dependence of the substituents was also observed in the living polymerization of isobutyl vinyl ether with the disubstituted versions, $TiCl_2(OR)_2$, with isopropoxy and phenoxy groups. The MWD of the polymers with $TiCl_3(OPh)$ was unimodal and relatively narrow ($\bar{M}_w/\bar{M}_n \sim 1.3$, Figure 5A). The $\bar{M}_n$ was in near agreement with the calculated value. Thus, living cationic polymerization with styrene is also feasible with $TiCl_3(OPh)$ in conjunction with **1** and nBu_4NCl, and the monosubstituted titanium(IV) chlorides with alkoxy and aryloxy groups have the moderate Lewis acidity suited for the living cationic polymerization of styrene.

A much stronger Lewis acid, $TiCl_4$, was also examined at −78 °C. Without nBu_4NCl, the **1**/$TiCl_4$ system induced an extremely rapid polymerization of styrene, even at a very low $TiCl_4$ concentration (10 mM), to give polymers with high molecular weights and broad MWDs (Figure 5B). Addition of nBu_4NCl into this system ($TiCl_4$/salt = 30/20 mM) still failed to give controlled polymers (Figure 5C), due to the difficulty in suppression of the free-ion species with such a strong Lewis acid as $TiCl_4$. The use of nBu_4NCl, molar excess over $TiCl_4$, ceased the polymerizations, probably because all the $TiCl_4$ changed into $TiCl_5^-$, an ineffective Lewis acid for styrene polymerizations. The polymerization of styrene with $TiCl_4$ is difficult to control because of its rather strong Lewis acidity and/or the higher R_p/R_i ratio than that with $TiCl_3(OiPr)$.[15c]

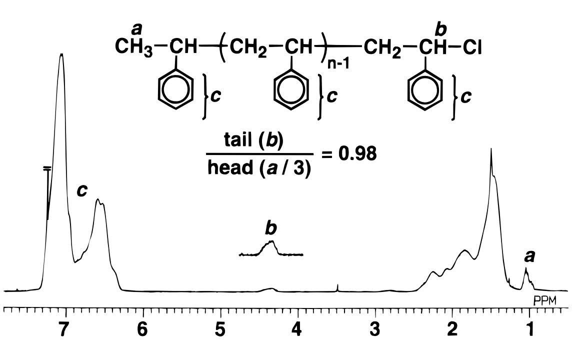

Figure 6. ^{1}H NMR spectrum of polystyrene obtained with **1**/$TiCl_3(OiPr)/nBu_4NCl$ in CH_2Cl_2 at −40 °C after quenching the polymerization with methanol at monomer conversion = 46%. $[M]_0 = 1.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[TiCl_3(OiPr)]_0 = 100$ mM; $[nBu_4NCl]_0 = 20$ mM.

On the other hand, the polymerizations with weaker Lewis acids, like $TiCl_3Cp$ (Cp = cyclopentadienyl) and $TiCl_2(OiPr)_2$, were much slower. The former induced a slow polymerization in CH_2Cl_2 at −15 °C in the absence of nBu_4NCl to give high molecular weight polymers (Figure 5D). The reaction with $TiCl_2(OiPr)_2$ was extremely slow, to give oligomers only, which is in contrast to the efficient living polymerization of vinyl ethers with the same compound.[13] Thus, the dialkoxytitanium dichloride is too weakly Lewis acidic for styrene polymerization.

^{1}H NMR Analysis of the Terminal Groups. The terminal structure of the living polymers with **1** and $TiCl_3(OiPr)$ was examined by ^{1}H NMR spectroscopy. Figure 6 shows the spectrum of the polymers obtained with **1**/$TiCl_3(OiPr)/nBu_4NCl$ in CH_2Cl_2 at −40 °C, followed by quenching with methanol.

In addition to the large absorptions of the main-chain methylene, methine, and phenyl (c) protons of the styrene units, the methyl protons (a) at the α-end were observed at 1.0 ppm. Absorptions assigned to the olefin (−CH=CHPh) or the indan termini were not observed even upon magnification of the spectrum. The signal at 4.3 ppm was ascribed to the chlorinated ω-terminal methine proton (b).[5b] The number-average end functionality ($\bar{F}_n$) of the chloride, determined by the peak area ratio of the ω-methine to the α-methyl protons, was close to unity. The DP_n determined from the peak intensity ratio of the methine b to the phenyl protons (c) (c/5b) was in close agreement with the calculated value based on the styrene/**1** mole ratio and also the value by size exclusion chromatography calibrated against standard polystyrene samples [DP_n = 26 (NMR), 23 (calcd), and 23 (SEC)]. These suggest that the living polymerization proceeds via activation of the carbon−chlorine bond (eq 1) and that the chlorine atom is attached to the terminal even after the quenching with methanol, as in the polystyrenes obtained with **1**/$SnCl_4/nBu_4NCl$.[16] Namely, the terminal chloride is not converted into isopropoxide by a possible ligand exchange reaction between the Lewis acid and the ω-terminal.[17]

In conclusion, living cationic polymerization of styrene has been achieved with titanium(IV) compounds, TiCl$_3$(OR) (R = *i*Pr, Ph), where their Lewis acidity is modulated by substitution of a chlorine atom in TiCl$_4$ with an electron-donating alkoxy or phenoxy group. In contrast, TiCl$_2$(O*i*Pr)$_2$, with a weaker Lewis acidity, was not effective in styrene polymerization, although it induced the efficient living polymerization of vinyl ethers. Thus, one of the keys to living cationic polymerizations of styrene is also the use of the Lewis acid, the strength of which is suitable for the reactivity of the monomers.

Experimental Section

Materials. Styrene (Wako Chemicals, purity > 99%) was washed with 10% aqueous sodium hydroxide and then with ion-exchanged water, dried overnight over anhydrous sodium sulfate, and distilled twice over calcium hydride under reduced pressure (~40 Torr) before use. CH$_2$Cl$_2$ (solvent) and bromobenzene (an internal standard for gas chromatography) were purified by the usual methods[13] and doubly distilled over phosphorus pentoxide and then over calcium hydride before use. 1-Phenylethyl chloride (**1**; Wako Chemicals, purity > 97%; racemic) was distilled twice under reduced pressure. TiCl$_4$ (Aldrich, 1.0 M solution in CH$_2$Cl$_2$), TiCl$_3$Cp (Aldrich, >97%), and *n*Bu$_4$NCl (Tokyo Kasei, >98%) were used as received. TiCl$_3$(O*i*Pr), TiCl$_2$(O*i*Pr)$_2$, and TiCl$_3$(OPh) were prepared and purified as already reported.[13]

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. The reaction was initiated by addition of a solution of TiCl$_3$(O*i*Pr) (in CH$_2$Cl$_2$, 0.50 mL) via a dry syringe into a monomer solution (in CH$_2$Cl$_2$, 4.5 mL) containing styrene (0.58 mL), **1**, and bromobenzene (0.12 mL) in CH$_2$Cl$_2$ at −40 °C. After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. Monomer conversion was determined from its residual concentration measured by gas chromatography with bromobenzene 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. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-802, K-803, and K-804) that were connected to a Jasco Trirotar-V precision pump and a Jasco 830-RI refractive index detector. The columns were calibrated against 10 standard polystyrene samples ($\bar{M}_n = 800-300\,000$; $\bar{M}_w/\bar{M}_n = 1.03-1.10$) as well as styrene oligomers (tetramer, trimer, and dimer) and monomer. ^{1}H NMR spectra were recorded in CDCl$_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column, Shodex K-2002).

References and Notes

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