

Rapid Stretching Vibration at Polymer Chain End

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Table of Contents

<Experimental Details>

<Supporting Figures and Table>

Figure S1. *para*-Aromatic ^{13}C NMR spectrum of non-deuterated PS.

Figure S2. Optimized molecular structures for three kinds of stereoisomers, isotactic (A), syndiotactic (B), and heterotactic (C), obtained by the M06 DFT/6-31G*.

Figure S3. Optimized molecular structures for isotactic, syndiotactic, and heterotactic isomers obtained by the B3LYP DFT/6-31G*.

Figure S4. Optimized molecular structure for syndiotactic 9mer of styrene obtained by the M06 DFT/6-31G*.

Table S1. Frequencies of C-D stretching vibrations for isolated styrene trimer computed at the B3LYP DFT/6-31G*.

Table S2. Frequencies of C-D stretching vibrations for isolated syndiotactic 9mer of styrene computed at the M06 DFT/6-31G*.

Experimental Details

Sample Preparation

Materials. Inhibitors in styrene (ST, Extra Pure Reagent, Nacalai Tesque Co., Ltd.) were adsorbed on activate aluminum oxide (particle size 2 - 4 mm, Kanto Chemical Co., Inc.) and removed. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich Chemical Co., Ltd.), 1-phenylethyl bromide (1-PEBr, 95%, Tokyo Chemical), CuBr (98%, Aldrich), deuterated styrene (D3-ST, 98%, Polymer Source Inc.), and tributyltin hydride (97 %, Merck Co., Inc.) were used as received. Anisole, toluene, and methanol were obtained from Nacalai Tesque Co., Ltd. (Extra Pure Reagent) and used without further purification.

Preparation of D3-M-PS ((A) in Figure 1). ST and D3-ST were copolymerized by atom transfer radical polymerization (ATRP) with CuBr / PMDETA complex and 1-PEBr as an initiator.¹ The initial molar composition of ST : D3-ST = 98 : 2. ST (2 mL, 17.4 mmol), D3-ST (40 μ L, 0.35 mmol), CuBr (25 mg, 0.174 mmol), PMDETA (36 μ L, 0.174 mmol), and 1-PEBr (24 μ L, 0.174 mmol) were admixed in a glass ampule. After degassing by a freeze-pump-thaw method, the ampule was

sealed in a vacuum. The sealed ampule was heated at 383 K. After the polymerization, the reaction mixture was precipitated from toluene solution to methanol. The D3-M-PS was filtered and dried in a vacuum at 353 K for 12 h. This procedure was repeated three times to remove impurities. The number average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) determined by gel permeation chromatography (GPC) were 11.0 kDa and 1.16, respectively.

Preparation of D3-E-PS ((B) in Figure 1). Non-deuterated PS ((C) in Figure 1) was polymerized first. The reaction procedure was completely the same with the D3-M-PS, but the D3-ST was not added. The PS was purified with the reprecipitation from the toluene solution to methanol. The M_n and M_w/M_n of the non-deuterated PS was 11.4 kDa and 1.25, respectively. Less than one D3-ST molecule was added to the chain end of the PS. The PS (2 g, 0.175 mmol), D3-ST (20 μ L, 0.175 mmol), CuBr (25 mg, 0.175 mmol), and PMDETA (37 μ L, 0.175 mmol) were dissolved in anisole (3 mL) and placed in a glass ampule. After degassing by a freeze-pump-thaw method, the ampule was sealed in a vacuum.

The sealed ampule was heated at 383 K for 4 hours. After the reaction, the ampule was opened and 0.5 mL (1.85 mmol) of tributyltin hydride was added to the solution.² After degassing by a freeze-pump-thaw method, the ampule was sealed again in a vacuum. The sealed ampule was heated at 383 K for 2 hours. The reaction mixture was dissolved in toluene and centrifuged to remove black precipitates. After that, the solution was poured into methanol. The precipitated sample was filtered and dried in a vacuum at 353 K for 24 h. This procedure was repeated more than three times to remove impurities. Little change in the M_n and M_w/ M_n by the reaction was detected by the GPC. However, the addition of the D3-ST was confirmed by FT-IR.

Measurements

Fourier Transform Infrared (FT-IR) Spectroscopy. Spectrum 400 FT-IR spectrometer manufactured by Perkin-Elmer was used for measurements. The temperature was controlled using temperature-variable cell, WEST 6100+ (Specac), calibrated using an external thermocouple. Measurements were performed with the transmission mode under nitrogen atmosphere with more than

25 scans at 2 cm^{-1} optical resolution. The data points were collected with 0.25 cm^{-1} digital resolution. The powder samples were molten on a KBr plate at 423 K in a vacuum; after bubbles in the sample were completely removed, the sample was covered with another KBr plate. The sample was further annealed at 393 K for one hour and cooled to a room temperature at the rate of 1 K min^{-1} in a nitrogen atmosphere. For the measurement of the PS / toluene solution, the solution containing 10 wt% of PS was injected between KBr plates with a 2 mm spacer. The transmittance mode was used and spectra were scanned more than 250. Band deconvolution was performed by using Igor software (WaveMetrics, Inc.).

Gel Permeation Chromatography. The M_n and M_w/M_n of the samples were determined by gel permeation chromatography (GPC) in THF (1mL/min) at 313 K on four polystyrene gel columns (Tosoh TSK gel GMH (beads size is $7\text{ }\mu\text{m}$), G4000H, G2000H, and G1000H ($5\text{ }\mu\text{m}$)) that were connected to a Tosoh CCPE (Tosoh) pump and a ERC-7522 RI refractive index detector (ERMA Inc.). The columns were calibrated against standard polystyrene (Tosoh) samples.

Nuclear Magnetic Resonance. NMR spectroscopy was performed on a JEOL

JNM-ECS 400 MHz. PS / deuterated chloroform solution with the concentration of 50 mg mL⁻¹ was contained in a 5 mm tube and used for the measurement.

Supporting Figures and Table

The stereoregularity of the PS polymerized by ATRP is determined from ^{13}C NMR signal of the *para*-aromatic carbon.³ The assignment of the peaks are shown in Figure S1. The composition of the syndiotactic, heterotactic, and isotactic triads are determined to 29, 69, and 2 %, respectively. The stereoregularity is almost the same with the PS synthesized by conventional radical polymerization.

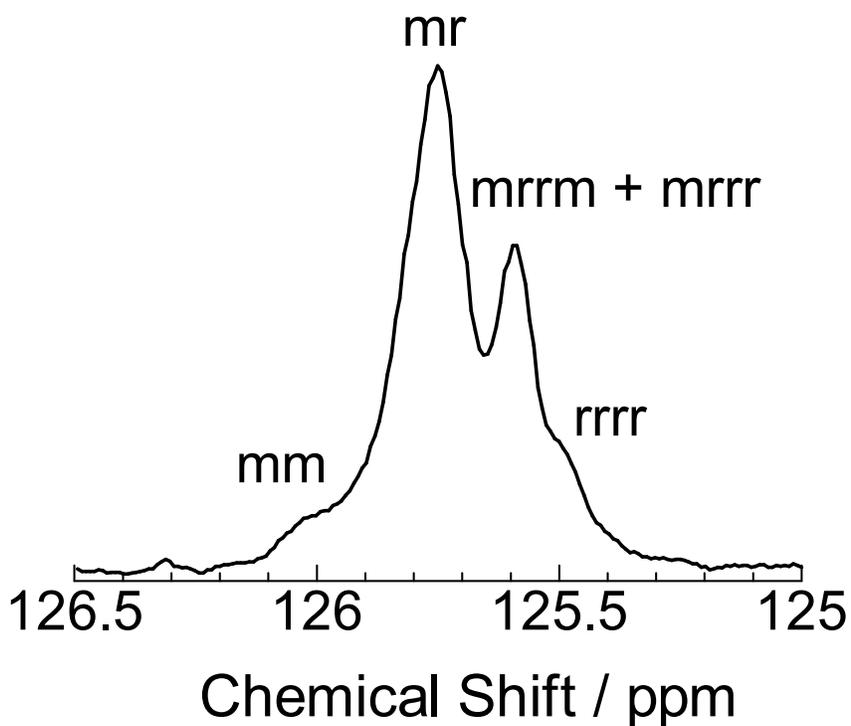
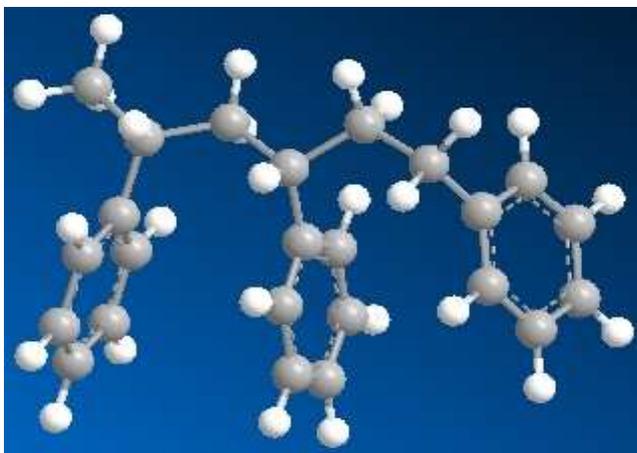
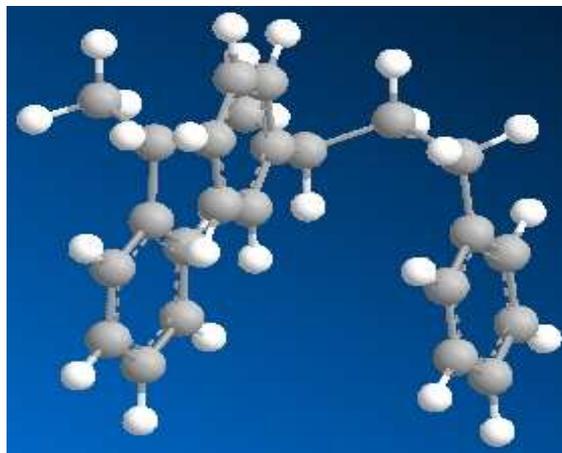


Figure S1. *para*-Aromatic ^{13}C NMR spectrum of non-deuterated PS.

(A) Isotactic



(B) Syndiotactic



(C) Heterotactic

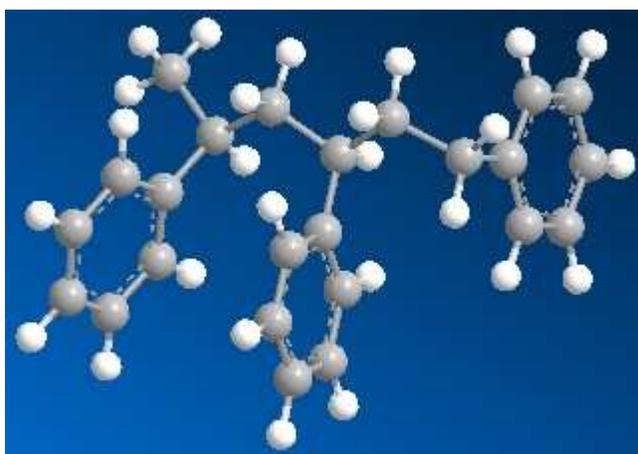
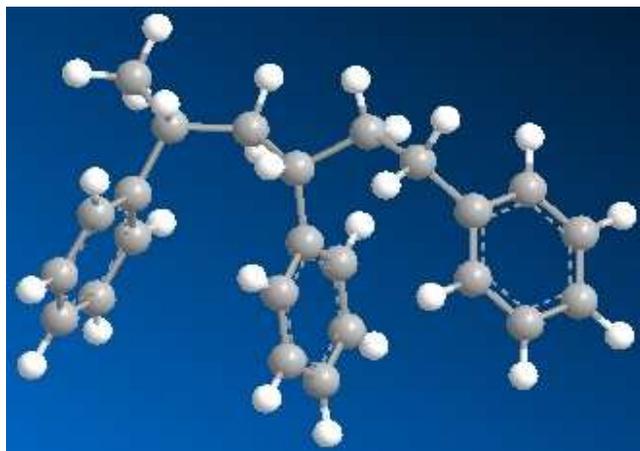
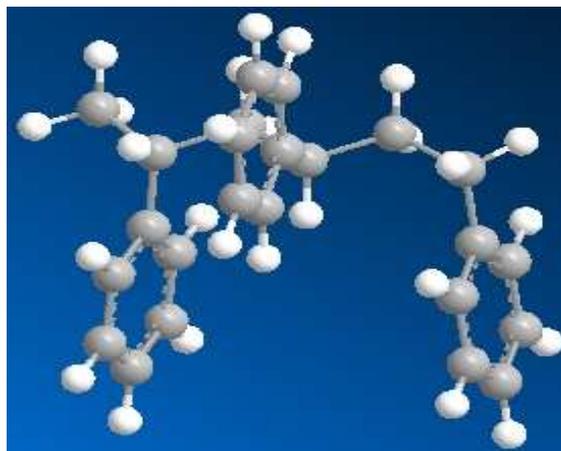


Figure S2. Optimized molecular structures for three kinds of stereoisomers, isotactic (A), syndiotactic (B), and heterotactic (C), obtained by the M06 DFT/6-31G*.

(A) Isotactic



(B) Syndiotactic



(C) Heterotactic

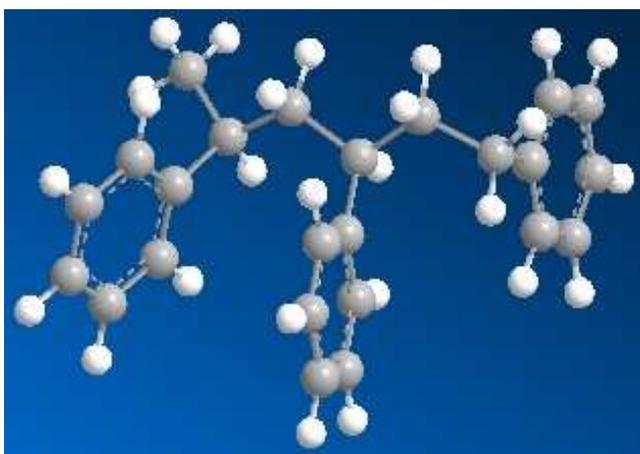


Figure S3. Optimized molecular structures for isotactic, syndiotactic, and heterotactic isomers obtained by the B3LYP DFT/6-31G*.



Figure S4. Optimized molecular structure for syndiotactic 9mer of styrene obtained by the M06 DFT/6-31G*.

Table S1. Frequencies of C-D Stretching Vibrations for Isolated Styrene Trimer Computed at the B3LYP DFT/6-31G*.

Tacticity	Deuterated Site	$\nu_{\text{as,CD}_2}$ / cm^{-1}	$\nu_{\text{s,CD}_2}$ / cm^{-1}	ν_{CD} / cm^{-1}
Isotactic	Center	2368.4	2295.8	2311.1
	End	2369.9	2297.3	2342.3
Heterotactic	Center	2367.7	2295.0	2323.2
	End	2368.9	2295.6	2354.9
Syndiotactic	Center	2361.0	2288.7	2341.6
	End	2367.6	2294.0	2354.1

Table S2. Frequencies of C-D stretching vibrations for isolated syndiotactic 9mer of styrene computed at the M06 DFT/6-31G*.

Tacticity	Deuterated Site	$\nu_{\text{as,CD2}}$ / cm^{-1}	$\nu_{\text{s,CD2}}$ / cm^{-1}	ν_{CD} / cm^{-1}
Syndiotactic	End	2368.5	2194.6	2252.6
	2nd from End	2259.9	2185.2	2231.3
	3rd from End	2260.8	2186.6	2231.8
	4th from End	2259.3	2184.4	2231.3
	Center	2259.8	2185.9	2231.3

References.

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- 2) Coessens, V.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 66 – 70.
- 3) Smith, L. M.; Coote, M. L. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 3351 – 3358.