

Supporting Information

Photo-induced Helix-Helix Transition of a Polystyrene Derivative†

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1.1 Experimental details

Materials and irradiation experiments. 2,2,6,6-Tetramethyl-4-piperidinol (TCI) was used as obtained. (*S*)-2-Methyl-1-butanol (TCI) was used as obtained. THF was distilled over CaH₂ under nitrogen and stored under nitrogen in the dark. CDCl₃ (Aldrich) was distilled over CaH₂ under nitrogen and stored under nitrogen in the dark. Irradiation experiments were conducted in a 1-mm or 1-cm quartz cell using an Ushio Optical Modulex SX-UID500MAMQQ 500 W Hg-Xe lamp at room temperature without any filter or polarizer.

Measurements. The ¹H NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer (400 MHz for ¹H measurement) and a JEOL JNM-ECA600 spectrometer (600 MHz for ¹H measurement). SEC measurements were carried out using a chromatographic system consisting of a Hitachi L-7100 chromatographic pump, a Hitachi L-7420 UV detector (254 nm), and a Hitachi L-7490 RI detector equipped with TOSOH TSK gel G3000H_{HR} and G6000H_{HR} columns (30 x 0.72(i.d.) cm) connected in series (eluent THF, flow rate 1.0 mL/min). SEC measurements were also performed using Wyatt Technology Dawn EOS-N MALLS detector and Viscotek Model TDA300 on-line RI and viscometric detectors. Right-angle scattering information was obtained from the MALLS detector and integrated into the TDA detector system to calculate molar masses and Mark-Houwink-Sakurada constants.

Absorption spectra were measured at room temperature with a JASCO V-550 and V-570 spectrophotometers. CD spectra were taken on a JASCO J-820 spectrometer. FT-IR spectra were measured using a ThermoFischer Scientific NICOLET6700.

AFM experiments were conducted at Yamagata University using a NanoScope IIIa under air on a Tapping mode. The polymer sample was dissolved in THF at 1.0×10^{-5} – 1.0×10^{-4} g/mL and spin casted on an HOPG substrate. The sample was dried under vacuum at room temperature for 2 h.

1.2 Heating experiments

A THF solution of the polymer in a 1-mm quartz cell (3.34×10^{-4} M per monomeric residue) was heated in an oil bath in the dark at 60 °C for 24 h. Also, a decalin solution of the polymer in a 1-mm quartz cell (3.34×10^{-4} M per monomeric residue) was heated in an oil bath in the dark at 150 °C for 24 h. Nitrogen gas was bubbled through the samples for 20 min immediately before heating. CD and UV spectra of poly(BMBPSt) before and after heating at 60 °C (left) and 150 °C (right) are shown in Fig. S1.

(A) at 60 °C in THF for 24 h

(B) at 150 °C in decalin for 24 h

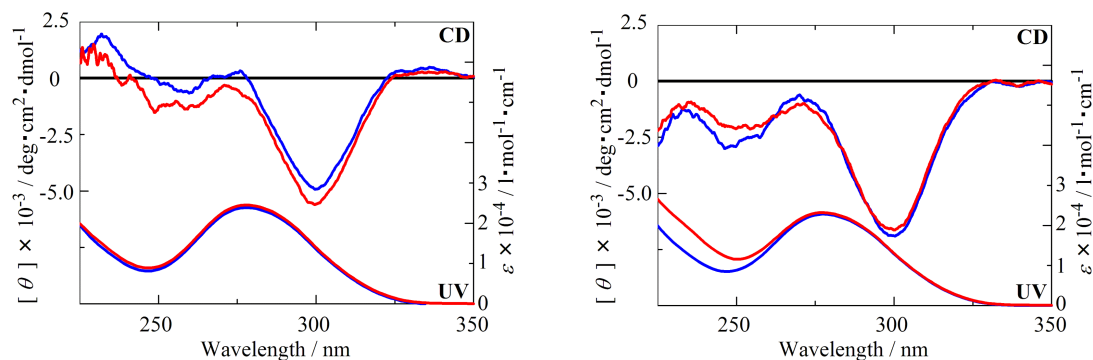


Fig. S1 CD and UV spectra of poly(BMBPSt) before (blue) and after (red) heating at 60 °C in a THF solution (A) and 150 °C in a decalin solution (B) under nitrogen for 24 h in the dark.

1.3 Irradiation in the air in the absence of scavenger

The polymer was dissolved in THF in a 1-mm quartz cell (3.34×10^{-4} M per monomeric residue), and the solution was irradiated under air. This sample was used for UV-CD measurements and SEC analyses. For the purpose of ^1H NMR measurements, the polymer (10 mg) was dissolved in 1 mL of CDCl_3 (not distilled) in a 1-cm quartz cell and irradiated under air. The results are shown in Figs. S2, S3, and S4. In Fig. S4, as a result of side-chain cleavage, the signals based on 2-methylbutanol and 2-methylbutene are observed.

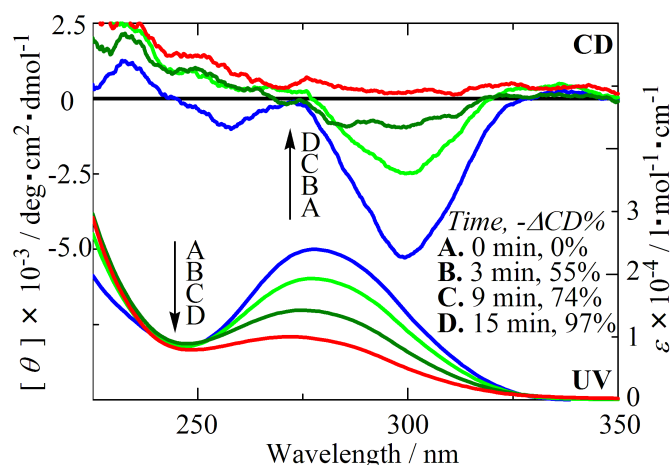


Fig. S2 Changes in CD and UV spectra of poly(BMBPSt) on photo irradiation with a 500 W Hg-Xe lamp for 0 min (A), 3 min (B), 9 min (C), and 15 min (D). (conc. = 3.34×10^{-4} M per monomeric residue, cell length 1 mm, in THF).

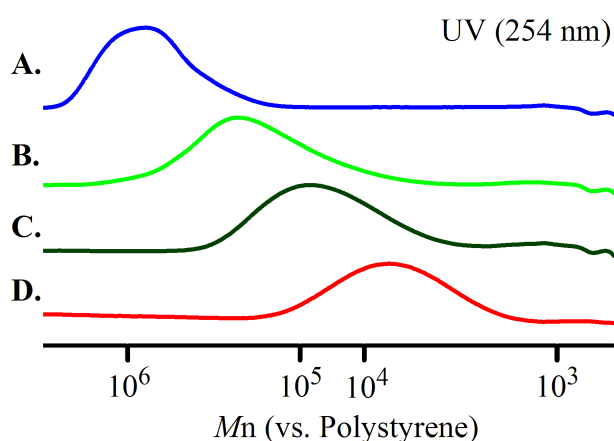


Fig. S3 Changes in SEC curves of poly(BMBPSt) on photo irradiation with a 500 W Hg-Xe lamp for 0 min (A), 3 min (B), 9 min (C), and 15 min (D). (conc. = 3.34×10^{-4} M per monomeric residue, cell length 1 mm, in THF).

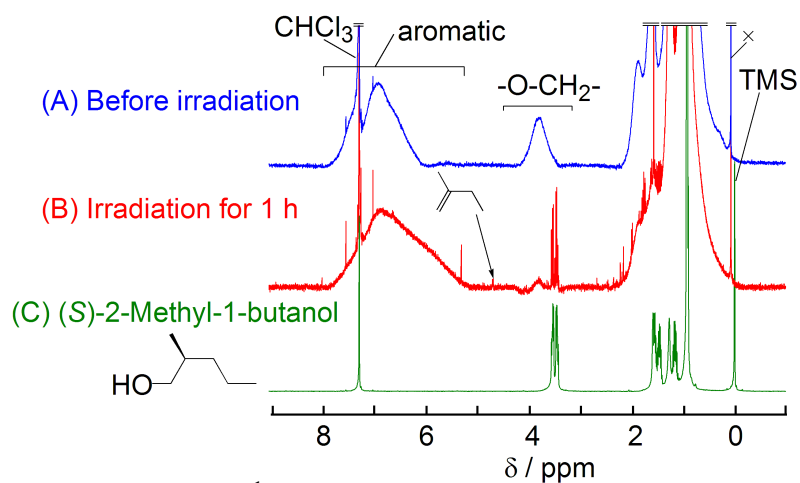


Fig. S4 400 MHz ¹H NMR spectra of poly(BMBPSt) before (A) and after (B) photo irradiation with a 500 W Hg-Xe lamp for 1 h in CDCl₃ (10 mg/ mL) under air, and that of (C) (S)-2-methyl-1-butanol. [CDCl₃, r.t.]

1.4 A Large-scale irradiation experiment

In order to identify whether the stereomutation takes place, we examined FT-IR, ^1H NMR, and SEC analyses of poly(BMBPSt) before and after irradiation for 81 h under nitrogen. The irradiation experiments were carried out in two 1-cm quartz cells containing ca. 7.8 mL sample. The cell samples were prepared by dissolving polymer in tetrahydrofuran (1.50×10^{-3} M) with 2,2,6,6-tetramethyl-4-piperidinol (1.50×10^{-2} M) as a radical scavenger, and irradiated by using a Hg-Xe lamp for 81 h under nitrogen. The polymer was isolated after irradiation by reprecipitation in methanol. The chemical structure was intact in the large-scale experiment as evidenced by FT-IR spectra (Fig. S5).

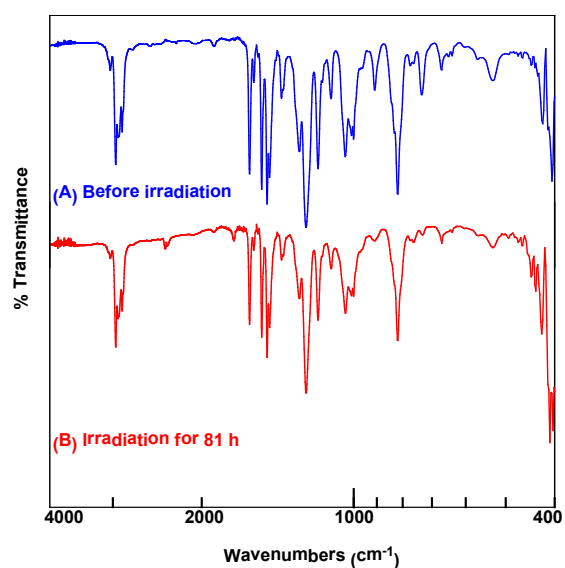


Fig. S5 FT-IR spectra of poly(BMBPSt) before (A) and after (B) irradiation for 81 h from a 500 W Hg-Xe lamp [KBr pellet]. Polymer was irradiated in a THF solution with the scavenger in a 1-cm quartz cell, removed scavenger and collected polymer by reprecipitation in methanol, and recovered by removing the solvent.

1.5 Structure of model monomeric unit

As a unit model, ethyl-2,5-bis[4-((*S*)-2-methylbutyloxy)phenyl]benzene structure was optimized by the semi-empirical AM1 method. The molecular edge-to-edge and ether oxygen-to-ether oxygen were measured as follows (Fig. S6).

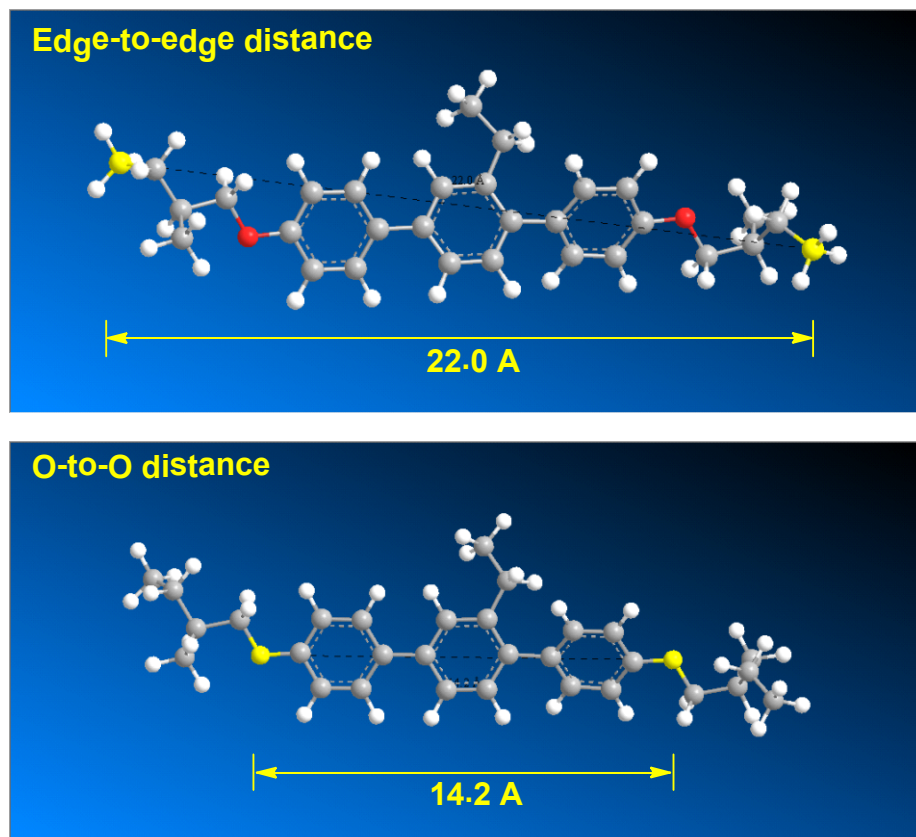
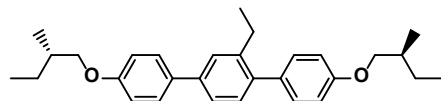


Fig. S6 Structure of ethyl-2,5-bis[4-((*S*)-2-methylbutyloxy)phenyl]benzene optimized by the AM1 method and distances between atoms.

1.6 Inspection of effects of the scavenger on CD spectra

In order to learn whether 2,2,6,6-tetramethyl-4-piperidinol as a radical scavenger affects CD spectra, the spectra of scavenger-free polymers before and after irradiation were taken (Fig. S7). The scavenger-free polymer was obtained by isolation after irradiation by reprecipitation in methanol for removed scavenger, and then dissolved in THF (3.34×10^{-4} M) in a 1-mm quartz cell. The spectra with and without the scavenger did not significantly differ, indicating that chiroptical properties of the polymer observed in this work are not affected by the presence of the scavenger.

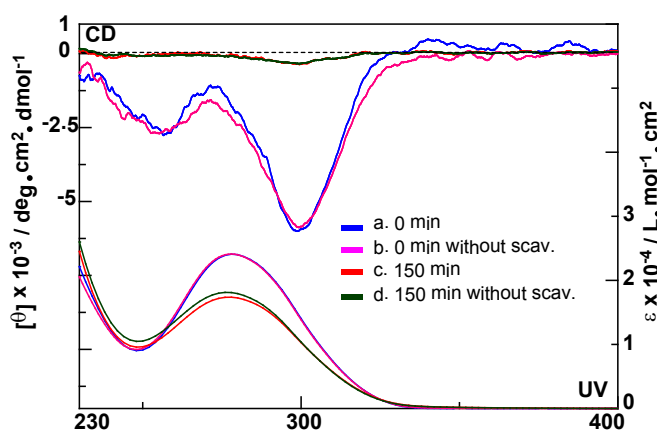


Fig. S7 CD and UV spectra of poly(BMBPSt) in a THF solution in the presence and absence of 2,2,6,6-tetramethyl-4-piperidinol as a radical scavenger before and after irradiation for 150 min: in the presence of scavenger before irradiation (a), in the absence of scavenger before irradiation (b), in the presence of scavenger after irradiation (c), in the absence of scavenger after irradiation (d). (conc. = 3.34×10^{-4} M per monomeric residue, cell length 1 mm, a 500 W Hg-Xe lamp).