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

Yue Wang,[a] Takeshi Sakamoto,[a] Yasuhito Koyama,[a] Yuma Takanashi,[b] Jiro Kumaki,[b] Jiaxi Cui,[c] Xinhua Wan,[c] and Tamaki Nakano[*a]

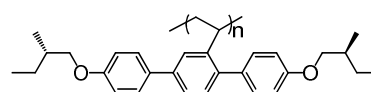**Poly(2,5-bis[4-((S)-2-methylbutyloxy)phenyl]styrene) having a helical conformation underwent helix-helix transition on photo irradiation. Conformational transition can significantly alter polymer properties, and so far thermal stereomutaion have been studied. However, as for photo-induced mutation, only helix-helix transition (irreversible CD-active to CD-silent helix transition) of a polyacrylate has been explored. Here, we present mutation of the polystyrene derivative. Chiroptical, viscometric, and vibrational spectroscopic analyses indicated the polymer mutated from an optically active helix to another, optically inactive helix with a different shape.**

Functions and properties of natural[1] and artificial[2] macromolecules are sensitive to chain conformation. For example, denaturation, mutation from a functional shape to a disordered one, of proteins makes them lose their precise functions.[2] Some artificial polymers undergo helix-helix transition governed by chemical, thermal and photo stimuli.[2-4] Such polymers revert their helix sense, showing a broad range of applications.[5-8] As the first artificial helical polymer which undergoes helix-helix transition by light and not by heat, we reported poly(2,7-bis(4-tert-butylphenyl)fluoren-9-ylacrylate) [poly(BBPFA)].[4,9]

A polystyrene derivative bearing a terphenyl structure in the side chain, poly(2,5-bis[4-((S)-2-methylbutyloxy)phenyl]styrene) [poly(BMBPSt)] (Chart 1) and its derivatives were synthesized by radical polymerization, and its preferred-handed helicity was evidenced.[10-12] This series of polymers contain terphenyl group in

the side-chain. Since the main-chain stereomutaion of poly(BBPFA) has been proposed to be triggered by twist-coplanar mutation[13] on excitation, we expected some main-chain mutation also on excitation of poly(BMBPSt). However, this polymer exhibited responses to light distinctive to those of poly(BBPFA). An optically active helix turned into an optically inactive, racemic helix where the shape helical chain remarkably changed, i.e., apparent chain length decreased and width of helix increased; the original slim helix became stocky by light.

Chart 1 Structure of poly(BMBPSt).

The polymer sample (M_n 79,320, M_w/M_n 2.01 vs. polystyrene) was prepared by radical polymerization in benzene at 60 °C according to the literature.[11] Photo irradiation to the sample was conducted using a 500 W Hg-Xe lamp without polarization. The sample was a solution in either tetrahydrofuran (THF) containing 2,2,6,6-tetramethyl-4-piperidinol[14] as an achiral radical scavenger. The scavenger was used to avoid any side reaction that could be caused by a radical species generated by irradiation.[14] The polymer solution in THF indicated intense Cotton effects in circular dichroism (CD) spectra attributable. The spectra are ascribed not to monomeric unit chirality but to a main-chain helix, because BMBPSt monomer shows CD spectra with much lower intensity and a completely different spectral shape from that of the polymer. The spectral intensity was not affected on heating at 60 °C for 24 h in THF and even at 150 °C for 24 h in decalin, indicating that the conformation is stable enough against heat (Fig. S1).

However, when a THF solution was irradiated at room temperature (ca. 23 °C), CD spectral intensity quickly and remarkably decreased and, eventually, the Cotton bands almost disappeared. Also, along with the change in CD, molar absorptivity in the UV spectra slightly decreased (hypochromism) (Fig. 1A).

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† Electronic supplementary information (ESI) available: Experimental details, ^{1}H NMR and optical spectra, SEC data, FT-IR and Raman spectra are available free of charge via the Internet at http://pubs.acs.org.
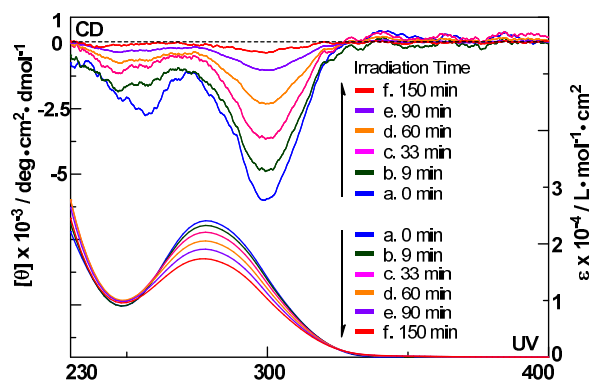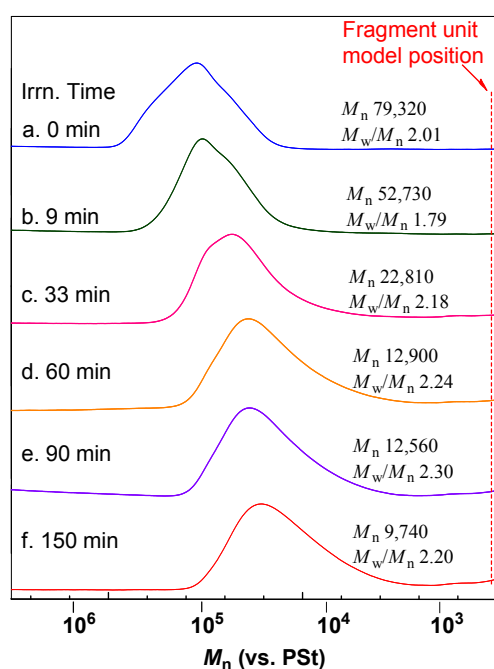
(A) CD-UV spectra

(B) SEC traces

Fig. 1 Changes in CD and UV spectra (A) and in SEC traces (B) of poly(BMBPSt) in a THF solution with 2,2,6,6-tetramethyl-4-piperidinol as a radical scavenger on photo irradiation with a 500 W Hg-Xe lamp for 0 min (a, blue), 9 min (b, green), 33 min (c, pink), 60 min (d, orange), 90 min (e, purple), and 150 min (f, red) at [BMBPSt] = 3.34 x 10^{-4} M per monomeric residue and [scavenger] = 3.18 x 10^{-3} M in a 1-mm quartz cell. The red dotted line in B indicates the elution position of 2,5-bis[4-hydroxy)phenyl]styrene as a model of possible fragment. M_n and M_w/M_n values were determined using polystyrene standard.

At the same time, apparent molar mass estimated by size exclusion chromatography (SEC) using polystyrene standards significantly decreased on irradiation where M_n after 150 min was smaller almost by an order of magnitude than the initial value while M_w/M_n values remained to be around 2 through the irradiation (Fig. 1B).

The decrease in molecular size was further confirmed by SEC analyses with a right-angle light scattering (RALS) and a viscometric detectors[15-17] which provide absolute molar masses, radius of gyration values (Rg), and Mark-Houwink-Sakurada

constants (α) of the polymer before and after irradiation. The following results were obtained: M_w, 360,900 (before irradiation) and 91,390 (after irradiation); Rg, 17.4 nm (before) and 8.4 nm (after); α, 0.78 (before) and 0.63 (after). The remarkable changes in M_w and Rg firmly supports that the size of the chain decreased. In contrast, the rather small change in α suggests that the major conformational characteristic remained through irradiation, i.e., helix is not destroyed. Thus, a possibility of helix-to-random coil transition leading to the CD intensity loss is ruled out.

^{1}H NMR spectra indicated broad signals due to the rigid helix of the polymer chain. On irradiation, overall signal shapes did not change though the relative intensity of the aromatic signals in the range 5～6 ppm only slightly increased (Fig. 2). These spectral features indicate that rigid helical structure is maintained through the above-described mutarotation and a decrease in molecular size detected by SEC.
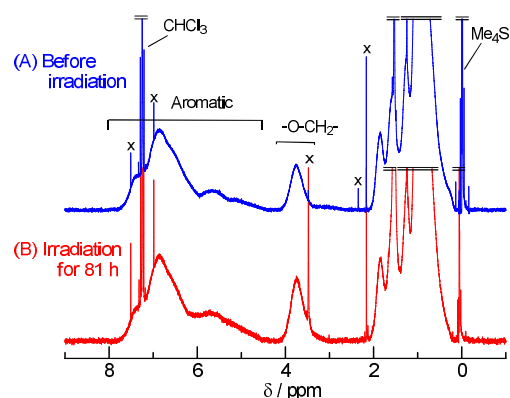

Fig. 2 ^{1}H NMR spectra of poly(BMBPSt) before (A) and after (B) irradiation for 81 h in a THF solution in the presence of 2,2,6,6-tetramethyl-4-piperidinol as a radical scavenger in using a 500 W Hg-Xe lamp at [BMBPSt] = 1.50 x 10^{-3} M and per monomeric residue and at [scavenger] = 1.50 x 10^{-2} M in a 1-cm quartz cell. The polymer was isolated after irradiation by reprecipitation in MeOH.

The loss of CD spectra thus is strongly indicative of a helix-helix transition leading to racemization of preferred-handed helix. The transition found here is not reversible as discussed later and leads to an optically inactive product (irreversible CD-active to CD-silent helix transition); it is discriminated from a reversible B-Z transition of DNAs without loss of optical activity which is also referred to as helix-helix transition.[18]

In rationalizing the observations, chain scission forming smaller molecules was ruled out because (1) no signal was observed at the position of 2,5-bis[(4-hydroxy)phenyl]styrene as a model of possible fragmentation product or the lower-molar-mass range in the SEC analyses (Fig. 1B), (2) molar mass dispersity did not largely change, and (3) no clear sharpening of signals due to the existence of shorter chains or smaller fragments of the chain to retard spin-spin relaxation was detected in the NMR spectra. Monitoring the stereomutation was attempted by FT-IR spectra. However, IR spectra did not indicate a clear change before and after irradiation, suggesting that the mutation does not significantly affect local vibrations (Fig. S5). This also supports that the chemical structure of the polymer is intact on irradiation.

These spectral and chromatographic changes hence can be ascribed to a conformational transition of the polymer chain.

The stereomutation was further examined by atomic force microscope (AFM) analyses. AFM has been shown to be an

effective tool in identifying and visualizing polymer helices.[2c,19] In the case of helical polyisocyanides,[20] polyacetylenes[21] and polymethacrylates,[22] helical shapes of chains have been clearly observed. Fig. 3 shows AFM profiles of the polymer before and after irradiation cast on an HOPG substrate by spin coating from a THF solution; for the profile after irradiation, the polymer was isolated from an irradiated solution to remove the scavenger.

The height and phase profiles of the polymer before irradiation indicated a texture consisting of string-like objects. Each string may arise from a helical chain of the polymer. The chains appear to be

(A) Before irradiation

(B) After irradiation

Fig. 3 Tapping mode AFM profiles of poly(BMBPSt) before (A) and after (B) irradiation for 81 h in a THF solution in the presence of 2,2,6,6-tetramethyl-4-piperidinol as a radical scavenger in using a 500 W Hg-Xe lamp at [BMBPSt] = 1.50 x 10^{-3} M and per monomeric residue and at [scavenger] = 1.50 x 10^{-2} M in a 1-cm quartz cell. The polymer was isolated after irradiation by reprecipitation in MeOH and was free from residual scavenger. The samples were spin-casted on an HOPG substrate from a THF solution at a concentration of 1 x 10^{-5} - 1 x 10^{-4} g/mL.

aligned in a single direction; chain alignments may have been governed by a stress applied to chains through spin coating the sample onto the substrate.

A distance of around 1.31 nm can be read for spacing of the string-like objects. This value seems reasonable for helix-helix spacing because, the distance between the phenolic oxygen atoms is ca. 1.42 nm in the monomeric unit (Fig. S6) which may represent the rough size of the widest, rigid part of the unit omitting the flexible alkyl groups.

The height and phase profiles of the polymer after irradiation also exhibited a texture consisting of string-like objects; however, two characteristics distinctive from textures before irradiation can be pointed out. First, the average height increased from 0.365 nm to 0.674 nm. Second, the distance for spacing of the string-like objects increased from 1.31 nm to 2.43 nm. These results along with the SEC data indicate that, when the polymer helix racemizes, it shrinks in length and fattens in width, i.e., a slim helix becomes a stocky helix.

Although no sufficient information is available at this stage, inter-chain interaction may have a role in the helix-helix transition and the structural change of the polymer chain. The changes in M_w and Rg might be correlated to dissociation of aggregated chains; however, because M_w/M_n did not largely change on irradiation, contribution of aggregation/dissociation, if any, would be insignificant.
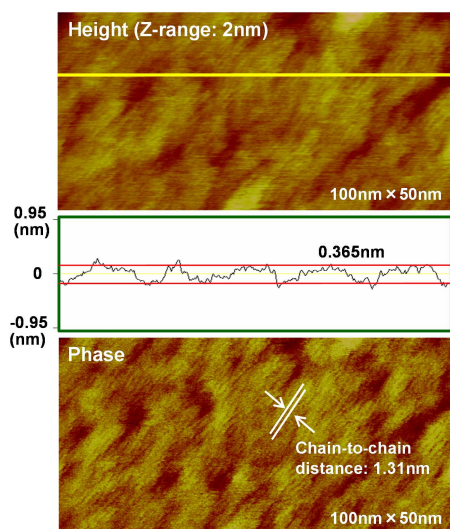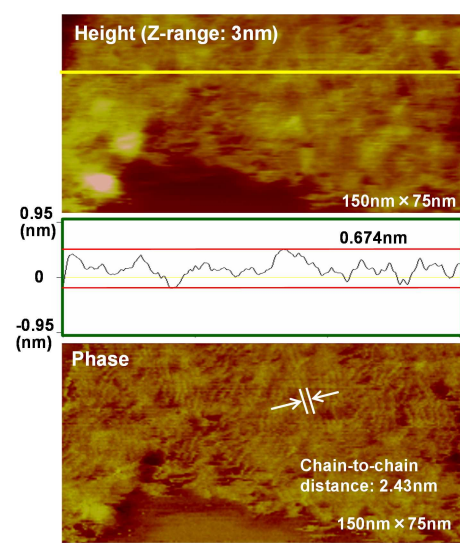
Considering all data presented so far, we propose the following conformational transition of the poly(BMBPSt) helix. The helix before irradiation was constructed in the process of polymerization ("the kinetic helix"). The kinetic helix is stable enough to survive heat stimulus. However, the kinetic helix is vulnerable to light stimulus and is transformed to a more stable, racemic helix ("the thermodynamic helix"). The activation energy between the kinetic and thermodynamic helices cannot be overcome by heating at up to 150 °C but by photo excitation. The emission bands of the Hg-Xe lamp used in this work which overlap the π-π* absorption band of the polymer are in the range of 254-313 nm corresponding to photon energies of 471-382 kJ/mol. The photon energy level seems to be sufficiently higher than energy provided by heating at 150 °C.

As mentioned earlier, poly(BBPFA) behaves similarly; however, a change in helical shape (slim or stocky) was not confirmed.[4,9] As in the case of poly(BBPFA), the helix-helix transition is assumed to be triggered by "twist-coplanar" transition of the side chain aromatic group.[4,9]

Back transformation of racemized, fattened helix to the original form was attempted by heating and irradiating with circularly polarized light. However, no clear recovery in CD spectra and SEC profiles were observed. The racemized helix appears to be very stable.

In summary, poly(BMBPSt) undergoes helix-helix transition transforming a preferred-handed helix formed by polymerization to a racemic helix on irradiation while the helix is stable on heating at 150 °C for 24 h. This is the first example of photo-induced helix-helix transition of a polystyrene derivative. This transition does not need any bond rearrangement such as bond scission or trans-cis isomerization around a double bond.[22,23] Although details of the mutation mechanism are yet to be explored by experiments and theoretical simulations,[24] we propose that the photo-induced conformational transition from a twist to coplanar in the side-chain terphenyl moiety triggers the stereomuation of the entire chain. The twist-coplanar transition has been reported for Ar-Ar compounds and macromolecules. Besides, only the Ar-Ar single bonds in the monomeric unit structure can be activated in rotation by light from a Hg-Xe lamp; the main-chain C-C bonds do not absorb light in the UV-Vis range. Based upon this rather small change in side-chain conformation can induce larger-scale transition of the main-chain.

Similar mechanisms have been proposed for photo-induced helix-helix transition of poly(BBPFA) and for CPL-assisted helix induction to a polyfluorene derivative.[25]

It should be noted that the polymer behaved differently on irradiation in the absence of the scavenger under air, i.e., the side-chain alkyl group came off in the form of 2-methylbutanol (Fig. S4). A photo reaction cleaving the alkyl-O bond seems to take place producing a phenol along with the conformational transition. In this case, the side-chain cleavage and the main-chain stereomutation can be taken as independent events since even without side-chain cleavage the main-chain mutation takes place as presented here.

Acknowledgements

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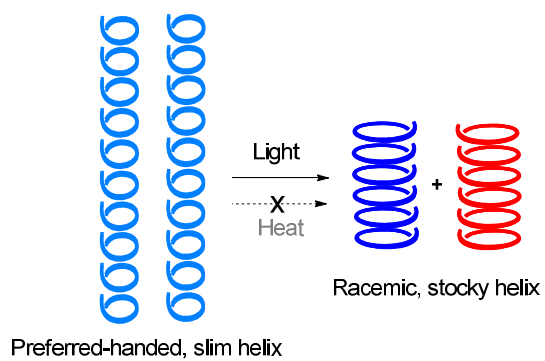
A novel photo-induced transition from a slim helix to a stocky helix along with helix racemization was found for an optically active polystyrene derivative for the first time.

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

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Contents

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 CaH_2 under nitrogen and stored under nitrogen in the dark. $CDCl_3$ (Aldrich) was distilled over CaH_2 under nitrogen and stored under nitrogen in the dark. Irradiation experiments were conducted in a 1-mm or 1-cm quarz cell using an Ushio Optical Modulex SX-UID500MAMQQ 500 W Hg-Xe lamp at room temperature without any filter or polarizer.

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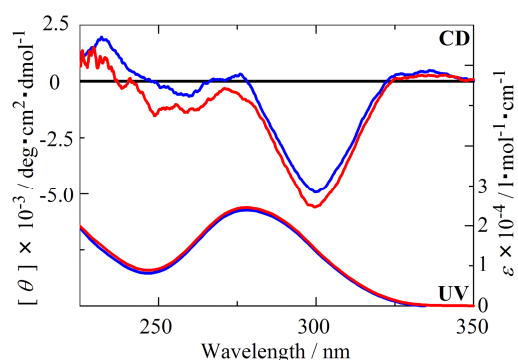
Absorption spectra were measured at room temperature with a JASCO V-550 and V-570 spectrophotometers. CD spectra were taken on a JASCO J-820 spectrometer. FT-IR spectra were measured using a ThermoFischer Scientific NICOLET6700.

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

(A) at 60 $^{\circ}$C in THF for 24 h   (B) at 150 $^{\circ}$C in decalin for 24 h
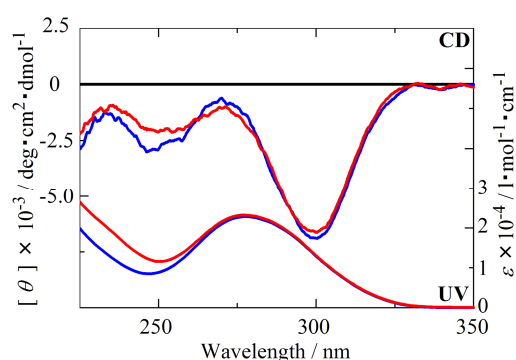

Fig. S1 CD and UV spectra of poly(BMBPSt) before (blue) and after (red) heating at 60 $^{\circ}$C in a THF solution (A) and 150 $^{\circ}$C in a decalin solution (B) under nitrogen for 24 h in the dark.

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 x 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 ^{1}H 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-methybutanol and 2-methybutene are observed.
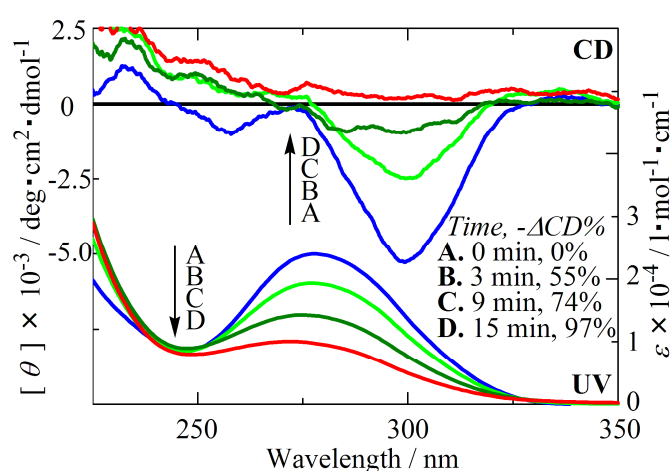
Fig. S2 Changes in CD and UV spectra of poly(BMBPSt) on photo irradiation with a 500 W Hg-Xe lamp for 0 min (A), 3 min (B), 9 min (C), and 15 min (D). (conc. = 3.34 x 10^{-4} M per monomeric residue, cell length 1 mm, in THF).
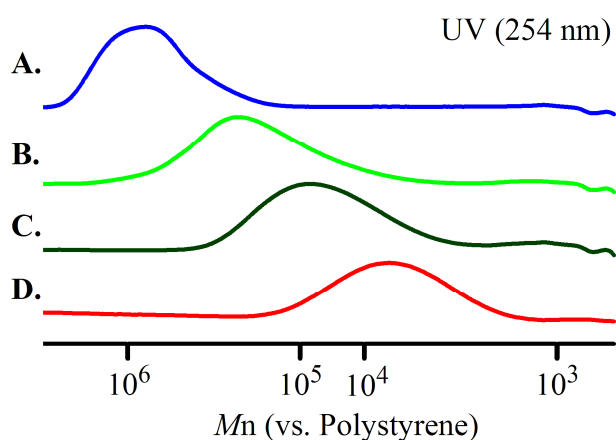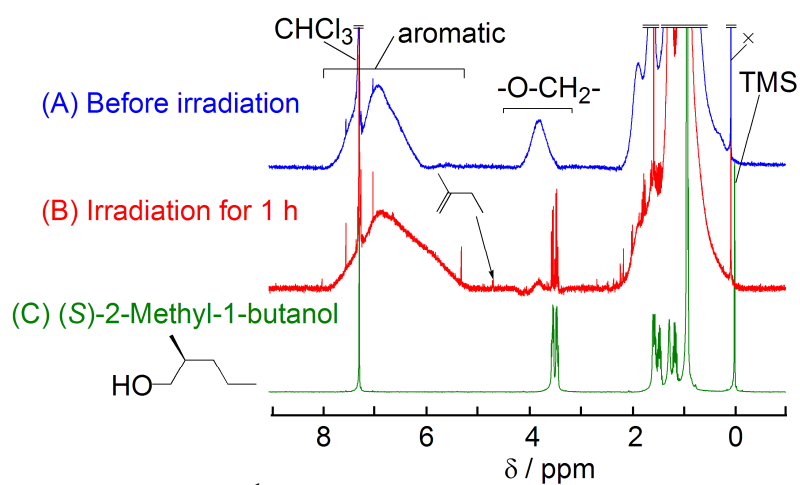

Fig. S3 Changes in SEC curves of poly(BMBPSt) on photo irradiation with a 500 W Hg-Xe lamp for 0 min (A), 3 min (B), 9 min (C), and 15 min (D). (conc. = 3.34 x 10^{-4} M per monomeric residue, cell length 1 mm, in THF).

Fig. S4 400 MHz ^{1}H NMR spectra of poly(BMBPSt) before (A) and after (B) photo irradiation with a 500 W Hg-Xe lamp for 1 h in CDCl$_3$ (10 mg/ mL) under air, and that of (C) (S)-2-methyl-1-butanol. [CDCl$_3$, r.t.]

1.4 A Large-scale irradiation experiment

In order to identify whether the stereomutation takes place, we examined FT-IR, ^{1}H 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 x 10^{-3} M) with 2,2,6,6-tetramethyl-4-piperidinol (1.50 x 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).
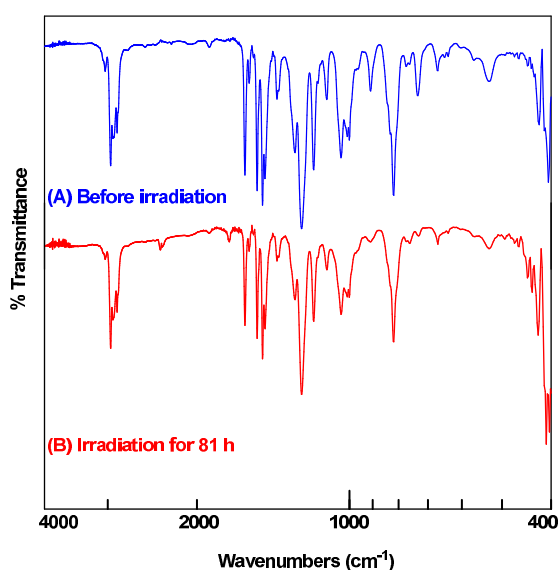

Fig. S5 FT-IR spectra of poly(BMBPSt) before (A) and after (B) irradiation for 81 h from a 500 W Hg-Xe lamp [KBr pellet]. Polymer was irradiated in a THF solution with the scavenger in a 1-cm quartz cell, removed scavenger and collected polymer by reprecipitation in methanol, and recovered by removing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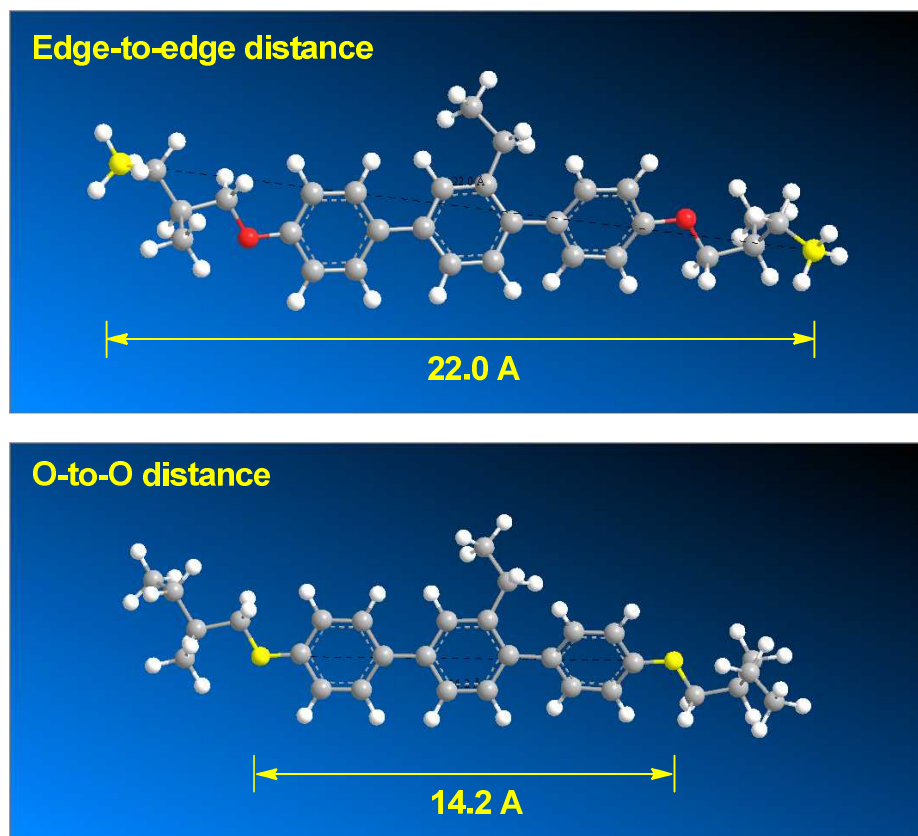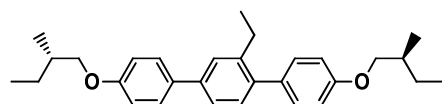

Fig. S6 Structure of ethyl-2,5-bis[4-((*S*)-2-methylbutyloxy)phenyl]benzene optimized by the AM1 method and distances between atoms.

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 spctra, 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.
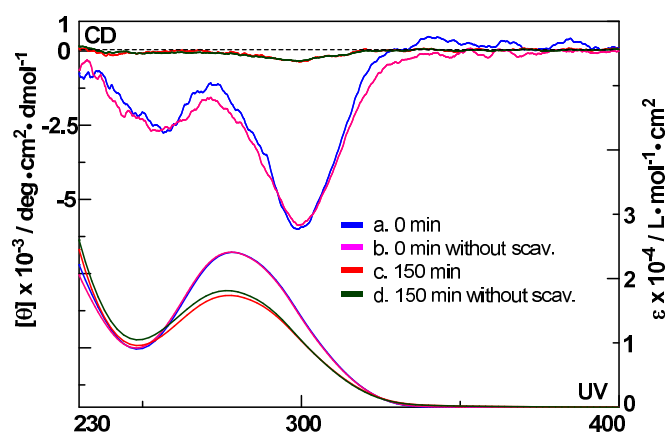

Fig. S7 CD and UV spectra of poly(BMBPSt) in a THF solution in the presence and absence of 2,2,6,6-tetramethyl-4-piperidinol as a radical scavenger before and after irradiation for 150 min: in the presence of scavenger before irradiation (a), in the absence of scavenger before irradiation (b), in the 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).