

## Isothianaphthene-Based Polymer with Triple Chiral Side Chains



Conductive Polymer

Kyoka Komaba, Hiromasa Goto\*

Department of Materials Science, Faculty of Pure and Applied Sciences,  
University of Tsukuba, Tsukuba Ibaraki 305-8573, Japan.

\*Correspondence: gotoh@ims.tsukuba.ac.jp

## ABSTRACT

Methine bridged conjugated polymers have low-bandgaps. This paper reports synthesis of methine-bridged type polyisothianaphthene bearing triple optically active substituents. We introduce chirality to the polymer. The polymer expects three advantages 1) main-chain low-bandgap, 2) isothianaphthene monomer repeat unit to show effective low-bandgap, 3) and good film forming property with chirality through good molecular packing. Infrared and UV-vis optical absorption measurements are carried out to confirm molecular structure.

**Keywords:** chiral, conductive polymer, isothianaphthene

## Introduction

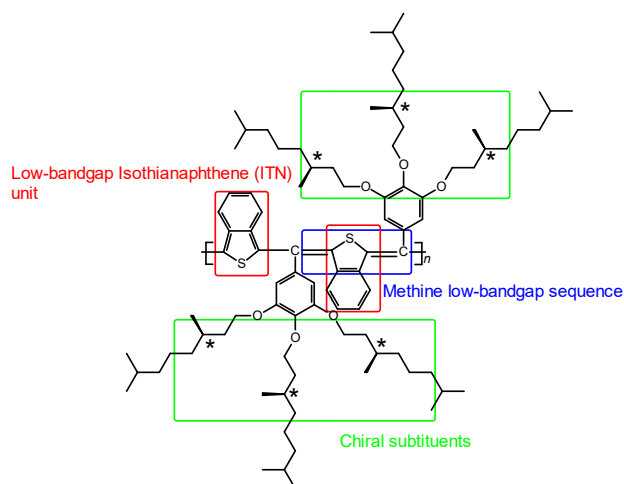
Various molecules with chirality exist in organism and many kinds of functions are expressed from the chirality<sup>2</sup>. Chirality is deeply related with biology<sup>3</sup>. Poly(arylene-methines) have been synthesized through reaction of arylenes and aldehyde groups with an aid of acid catalyst to obtain low-bandgap polymers.<sup>4</sup>

In this research, a low-bandgap polymer with chirality was synthesized by introducing six chiral alkyl side chains into an isothianaphthene based methine bridge backbone. Molecular structure and functions are displayed in Fig. 1. The polymer has 1) sequence of methine structure as main-chain low-bandgap, 2) isothianaphthene low-bandgap repeat unit to show effective low-bandgap, 3) and good film forming property with chirality through good molecular packing. In other words, the polymer has innovative characters as monomer unit and main chain low-bandgap function, and triple chiral substituents with six chiral centers in the monomer repeat unit.

## Experiment

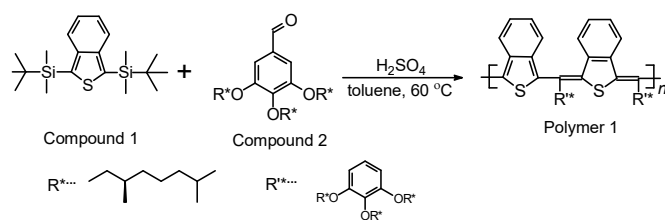
Into a flask were added compound 1 (209 mg, 0.331 mmol), compound 2 (109 mg, 0.301 mmol), and sulfuric acid (304.1 mg, 3.10 mmol) in toluene (1.0 mL) under argon atmosphere.

After stirring at 60 °C for 24 h, the reaction mixture was poured into excess amount of methanol. The precipitate was collected by filtration, and the solvent was removed under vacuum to afford black powder (276 mg, 0.200 mmol, Y = 66%), Scheme 1. The polymer thus synthesized is abbreviated as *Poly1*.

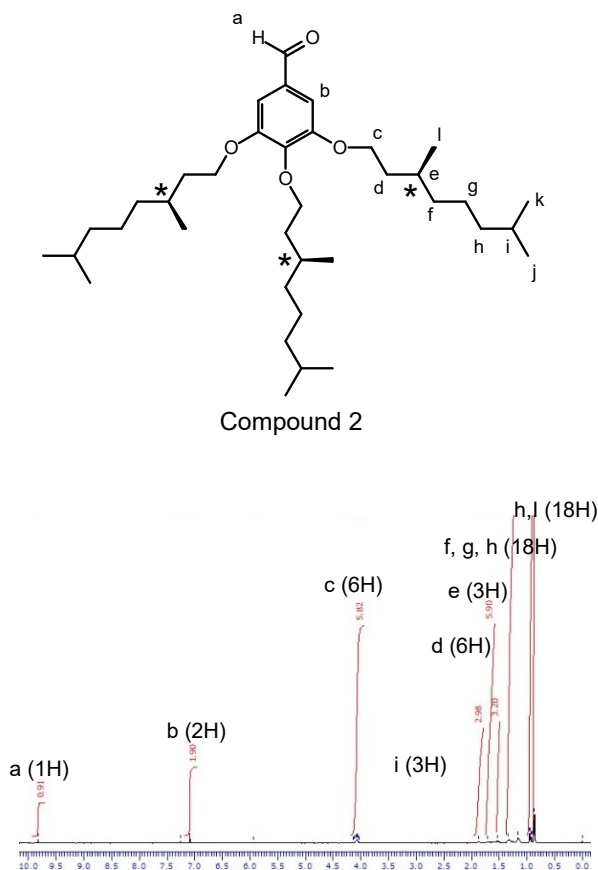


**Fig. 1.** Molecular structure and functions.  
\* = stereogenic center.

Conductive Polymer

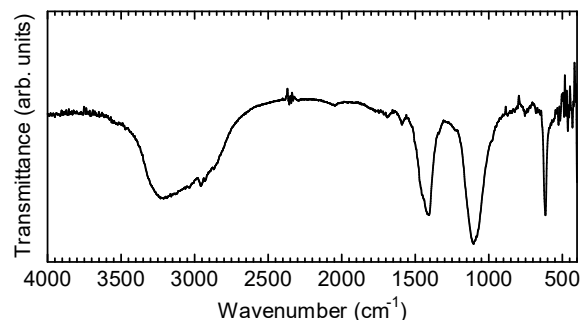
Scheme 1. Synthesis of *Poly1*.

## Results and Discussion

Fig. 2.  $^1\text{H}$  NMR spectrum of compound 2.

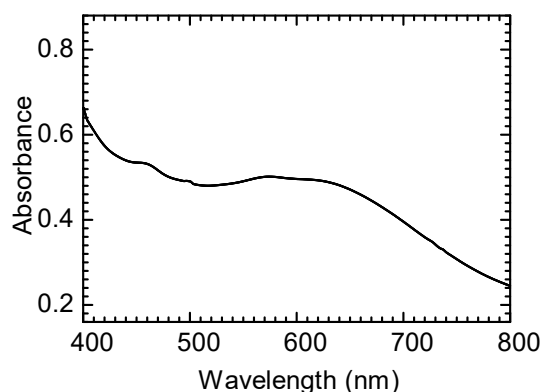
$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ; TMS):  $\delta$  0.87 (t, 18H,  $\text{C}_6\text{H}_{13}\text{-CH}_2\text{-CH}_3$ ,  $J = 6.8$  Hz), 1.17-1.23 (m, 18H,  $\text{C}_2\text{H}_4\text{-CH}(\text{CH}_3)\text{-C}_3\text{H}_6\text{-C}_3\text{H}_7$ ), 1.53 (m, 3H,  $\text{C}_2\text{H}_4\text{-CH}(\text{CH}_3)\text{C}_6\text{H}_{12}$ ), 1.71 (m, 2H,  $\text{CH}_2\text{-CH}_2\text{-C}_8\text{H}_{17}$ ), 1.87 (m, 6H,  $\text{C}_6\text{H}_{13}\text{-CH}_2(\text{CH}_3)\text{-CH}_3$ ), 4.07 (m, 6H,  $\text{CH}_2\text{-C}_9\text{H}_{19}$ ), 7.09 (dd, 2H, 2,6-H (benzene),  $J = 8.0$  Hz), 9.83 (s, 1H, -CHO)

Compound 2 was measured with the NMR. The NMR result is shown in Fig. 2.

Fig. 3. Infrared absorption spectrum for *Poly1*.

Infrared absorption spectrum for *Poly1* is shown in Fig. 3. The C-H stretching vibration in alkyl chains is observable at  $3211\text{ cm}^{-1}$ . The C=C stretching vibration of main chain is shown at  $1407\text{ cm}^{-1}$ . C-O stretching vibration is observable at  $1103\text{ cm}^{-1}$ . The bending vibration signal of C-H is observed at  $615\text{ cm}^{-1}$ .

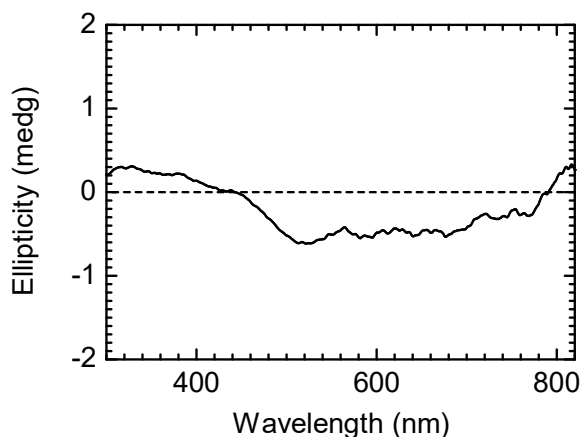
### UV-vis absorption and CD

Fig. 4. UV-vis optical absorption spectrum of *Poly1* in tetrahydrofuran (THF) solution.

### Infrared absorption

Fig. 4 shows the UV-vis optical absorption the spectrum in dilute solution of tetrahydrofuran (THF). Trace amount of *Poly1* was dissolved in THF. The UV-vis absorption shows that *Poly1* has absorption band at 574 nm. This absorption is derived from  $\pi\text{-}\pi^*$  transition of the main chain of the isothianaphthene-methine sequence. The polymer shows very weak CD signal, implying the main chain is rigid and forms loose helical structure (Fig. 5). Chiral side chains have distance from the main chain and provide weak induction to form main chain helical structure. UV-vis absorption and CD measurements were no carried out in film state

because polymer film could not be prepared by drop cast.



**Fig. 5.** Circular dichroism (CD) spectroscopy measurement result for *Poly1*.

### Conclusions

Synthesis of isothianaphthene based conductive polymer with chiral side chains was succeeded. This polymer is soluble in tetrahydrofuran. The chiral side chain can contribute formation of good cast film for applications such as electro-opto-functional films.

### Acknowledgment

We thank Y. Innami for synthesis of chiral compounds.

### References

- (1) Inaki, M; Sasamura, T; Matsuno, K., Cell Chirality Drives Left-Right Asymmetric Morphogenesis, *Front. Cell Dev. Biol.* 03, April, **2018**.
- (2) Dyakin, V. V.; Lucas, J.; Dyakina-Fagnano, N. V.; Posner, E. V.; Vadasz, C. The Chain of Chirality Transfer as Determinant of Brain Functional Laterality, *Neurol. Neurosci. Res.*, **2017**, 1(1), 2.
- (3) Tverdislov, V. A.; Malyshko, E. V.; Il'chenko, S. A.; Zhulyabina, O. A.; Yakovenko, L. V. A Periodic System of Chiral Structures in Molecular Biology. *Biophys.* **2017**, 62 (3), 331–341.
- (4) Chen, W. C.; Jenekhe, S. A., Small-Bandgap Conducting Polymers Based on Conjugated Poly(heteroarylene methines). 2. Synthesis, Structure, and Properties, *Macromol.*, **1995**, 28, 465-480.

Received: 2019.11.3

Accepted: 2019.12.11