

論文 / 著書情報
Article / Book Information

題目(和文)	固相系で機能する光および熱応答性ロタキサンスイッチの合成と応用
Title(English)	Synthesis and Application of Photo- and Thermoresponsive Rotaxane Switch Working in the Solid State
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10124号, 授与年月日:2016年3月26日, 学位の種別:課程博士, 審査員:高田 十志和,柿本 雅明,小坂田 耕太郎,石曾根 隆,大塚 英幸
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10124号, Conferred date:2016/3/26, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

論文の要約

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論文題目：固相系で機能する光および熱応答性ロタキサンスイッチの合成と応用

Thesis Title: Synthesis and Application of Photo- and Thermoresponsive Rotaxane Switch Working in the Solid State

This thesis contains five chapters. Aiming to develop novel rotaxane switch systems directed toward the application to polymer systems, the author has studied rotaxane switches triggered by photoisomerization and thermochemical decomposition. The switching behavior was studied not only in solution state but also in solid state, suitable to polymeric materials. Furthermore, a thermoresponsive rotaxane switch was introduced into the side chain of polyphenylacetylene. The reversible structural change of the polymer main chain owing to the precise control of the rotaxane switch in solid state ensured the potential application of such a rotaxane switch.

In chapter 1 “Introduction”, the background for rotaxanes including rotaxane switch driven by various stimuli such as acid/base, light, redox, and ion is described. Some polymer systems controlled by rotaxane structures in the main chain or side chain were introduced as the previous work. In general, chemical stimulus often reduces the responsibility of rotaxane switch by the accumulation of salts in acid/base stimulus system in the recycle use. In the case of electrochemical stimulus, the structural versatility is quite limited. In order to overcome these limitations of rotaxane switch, the author designed and synthesized novel photoresponsive rotaxane switch based on spiropyran moiety and thermoresponsive rotaxane switch triggered by thermal decomposition of trichloroacetic acid (TCA) directed toward solid-state application. Considering these circumstances, the purpose of this work is described.

In chapter 2 “Synthesis of spiropyran-conjugated rotaxane switch and its photoisomerization”, a spiropyran-end-capped *sec*-ammonium-type rotaxane are described. The photo-induced isomerization of spiropyran to zwitterionic merocyanine was controlled by the switching of the rotaxane moiety. Moreover, the spiropyran-based rotaxane dispersed in PMMA was prepared and this polymer film showed a clear color change owing to the photoresponsive rotaxane. The switching behavior in the form of the merocyanine moiety of the rotaxane was discussed.

In chapter 3 “Thermally responsive rotaxane switch triggered by thermally-degradable conteranion in solid state”, the author described the synthesis of two *tert*-amine-type rotaxanes by urethane end-cap method and the end-cap via the [2+3] nitrile *N*-oxide / acetylene cycloaddition, and their characterization as the molecular switch working in solid state. After acidification of the amine moiety with trichloroacetic acid (TCA) by grinding in solid state, the successful positional movement of the wheel component in solid state was confirmed, which the heating of the resulting rotaxane yielded the originated *tert*-amine-type rotaxane.

In chapter 4 “Syntheses and solid-state control of polyphenylacetylene possessing a thermoresponsive rotaxane switch in the side chain”, synthesis of polyphenylacetylene having the thermoresponsive rotaxane switch in the side chain and helical structure control of the polyphenylacetylene main chain by the rotaxane switch are described. When the polyphenylacetylene film on a glass plate was heated to anion-decomposed temperature, the film color was dramatically changed from brown to red. This indicated that the positional switch of the rotaxane moiety promptly changed the helical pitch of the polyphenylacetylene main chain to lengthen the effective conjugation length in film state. Meanwhile, the heating of the film showing red color was dipped into a TCA solution in *n*-hexane to form the yellow-colored film again. Thus, thermoresponsive polymer system triggered by rotaxane switch has been developed.

In chapter 5 “Conclusion”, the results obtained in this work are summarized. Further applications of the rotaxane switch are proposed.