論文 / 著書情報
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題目(和文)	ロタキサン構造形成を基盤とした超分子液晶の設計と相転移挙動
Title(English)	Design of Supramolecular Liquid Crystals Based on Rotaxane Structure Formation and Their Phase Transition Behavior
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Supramolecular liquid crystals (LCs), LCs constructed using non-covalent bonds, are able to create material functions that enhance the properties of the introduced non-covalent bonds and take broader molecular design approaches to the emergence of LC properties. In the field of supramolecular chemistry, rotaxanes and pseudorotaxanes, wherein axle-shaped molecules thread ring-shaped molecules, have attracted attention for their ability due to their dynamic material functions derived from their unique threaded architecture. Supramolecular LCs with rotaxane/pseudorotaxane structures are expected to provide novel high-performance materials. However, only a few LC rotaxanes have been synthesized and their molecular design concept is limited. Notably, LC pseudorotaxanes have not been reported yet. In this thesis, the author presents a novel design of supramolecular LCs based on a rotaxane structure. The LC properties of this design arise from the formation of a threaded structure with an axle molecule and ring molecule. After demonstrating the LC molecular design concept through a [2]rotaxane synthesis, this design concept was extended to realize LC pseudorotaxanes and LC supramolecular polymers with rotaxane structures. Furthermore, a designed LC pseudorotaxane exhibited thermally induced phase transition behavior reflecting the reversible associations and dissociation of pseudorotaxane structure, in addition to LC phase expression.

In Chapter 2, the author synthesized an LC [2]rotaxane by integrating an axle molecule as mesogen core and a ring molecule as flexible tail via a threaded structure. The prepared control molecules with partially different molecular structures from that of the synthesized LC [2]rotaxane revealed the integration of mesogen core and flexible tail via a threaded structure enabled the LC phase emergence.

In Chapter 3, the author designed LC pseudorotaxanes utilizing the design concept

demonstrated in Chapter 2. By mixing an axle molecule as mesogen core and a ring as flexible tail in a solvent and then evaporating, solid-state [2]pseudorotaxanes with smectic-like structure were formed. Through the discussion of phase transition behavior in terms of the structure, polarity, and thermal properties of the constituent axle and ring molecules, the author performed an LC [2]pseudorotaxane with thermally stable phase transition.

In Chapter 4, the author performed LC pseudorotaxane design involving hydrogen bonding. An axle molecule with a dual function of threading structure formation and hydrogen bond acceptor afforded an LC pseudorotaxane with carboxylic acids and a ring as flexible tail. By selecting the carboxylic acids, this design concept enabled the synthesis of LC supramolecular polymers with pseudorotaxane structures in both main and side chain types.

In Chapter 5, the author designed a [2]pseudorotaxane exhibiting thermally induced phase transitions exhibiting liquid-liquid phase separation, as well as LC phase. This phase separation was a lower critical solution temperature (LCST) type. The combination of liquid-liquid and liquid-LC phase separation created a unique three-layer structure on the micrometer scale. The thermodynamic, optical, and diffusional studies revealed that this unique phase separation behavior is a novel phenomenon of LC pseudorotaxane causing reversible dissociation and reassociation.

The author developed a novel molecular design concept integrating mesogen core and flexible tail by the formation of a threaded structure. Based on the concept, a series of LC supramolecules with rotaxane/pseudorotaxane structures were successfully created. Besides the synthesis, a unique thermally induced liquid-liquid phase separation behavior utilizing the pseudorotaxane characteristics was elucidated. The author

believes that this research contributes to the development of a new supramolecular LC material field combining rotaxane structure and LC properties, leading to the fabrication of highly functional materials.