博士論文

Development of Self-Assembled Nanostructured Liquid Crystals for Transport and Separation

（輸送・分離に向けた自己組織化ナノ構造液晶の開発）

濱口　和馬

Chapter 1. Introduction

Functional materials for transport and separation have attracted increasing attention in modern society. Ensuring safe water is one of the most urgent global issues. Membrane technologies for water treatment, such as desalination and virus rejection, are essential for obtaining high-grade and safe water. Energy transformation toward sustainable society is also an important challenge. Electrolytes for energy devices such as lithium-ion batteries and fuel cells are intensively studied. Construction of ordered nanostructures using molecular self-assembly is a promising approach to achieve higher performances for these materials.

Liquid crystals are self-assembled materials that combine the fluidity of liquids and the order of crystals. They have been intensively studied as functional materials due to their ordered structures and dynamic properties. Recently, liquid crystals with well-defined structures in nanometer scale have been applied in various fields. Amphiphilic liquid crystals can self-assemble into various nanostructures through nanosegregation, which can be controlled by molecular design. These nanostructured liquid crystals can form ordered nanochannels with assembled functional moieties. The nanochannels are expected to exhibit promising functions for transport and separation. The author focused on the use of the nanochannels as mass transport pathways of water-treatment membranes and electrolytes. Non-conventional molecular design and control of nanostructures are necessary for further functionalization of these liquid-crystalline (LC) materials.

In the present thesis, development of nanostructured liquid crystals for transport and separation utilizing molecular self-assembly is described. Introduction about molecular designs for LC materials showing functions of transport and separation is presented in chapter 1. In chapters 2 and 3, the development of nanostructured liquid crystals for water-treatment membranes, focusing on the use of nanochannels as water transport pathways is described. Gemini ionic liquid crystals (chapter 2) and two-component columnar liquid crystals (chapter 3) are newly designed and synthesized for construction of LC nanostructured water-treatment membranes. In chapter 4, using LC nanochannels as ion transport pathways, ion-conductive liquid crystals that exhibit unique reentrant phase transitions have been reported.

Chapter 2. 2D Nanostructured Water-Treatment Membranes Based on Gemini Ionic Liquid Crystals

In this chapter, the development of 2D nanostructured water-treatment membranes based on gemini smectic liquid crystals is described. Polymer-based water-treatment membranes are essential for obtaining high-quality water with lower energy consumption. Nanostructured liquid crystals are attractive candidates for water-treatment membranes because their precisely controlled nanochannels are beneficial for efficient water transport. In this context, thermotropic gemini smectic liquid crystals have been designed and synthesized for 2D nanostructured water-treatment membranes. Two monomeric amphiphiles containing an imidazolium moiety and a polymerizable alkyl chain are laterally connected to obtain cross-linkable gemini LC monomers. One of the gemini monomers exhibits a smectic LC phase with 2D ionic nanochannels. The layered nanostructure of the gemini LC monomer has been successfully preserved by photopolymerization in the smectic phase, yielding a self-standing polymer film. X-ray diffraction (XRD) measurements confirm that the smectic nanostructure is maintained before and after photopolymerization. A water-treatment membrane containing the polymerized 2D nanostructured thin film as a separation layer has been prepared. Virus filtration experiments have revealed that the 2D nanostructured membrane can reject viruses in water over 99.99997%. In addition, the 2D nanostructured membrane shows higher water permeability than previously reported water-treatment membranes based on thermotropic ionic liquid crystals. The high virus rejection is due to the suppression of pinholes by the fixation of fluid smectic phases. The increase in water permeability results from the formation of uniform 2D ionic nanochannels that are beneficial for water transport. Salt rejection properties are also examined by filtrating aqueous solutions of NaCl and $MgSO_4$. The 2D nanostructured membrane exhibits higher rejection of NaCl than that of $MgSO_4$, although NaCl is smaller than $MgSO_4$. This selectivity is similar to those of the LC nanostructured membranes with 1D and 3D ionic nanochannels. On the other hand, the rejection rates of the 2D nanostructured membrane are lower than those of 1D and 3D nanostructured membranes. These results lead to the conclusion that the dimension of ionic nanochannels affects salt rejection rate but not selectivity.

Chapter 3. Nanostructured Water-Treatment Membranes Using Two-Component Columnar Liquid Crystals

Construction of columnar LC nanostructured water-treatment membranes utilizing two-component liquid crystals is described in this chapter. In earlier studies, LC nanostructured water-treatment membranes have been prepared from one-component liquid crystal and their channel sizes are limited to less than 1 nm. Material design in this chapter is to enlarge the channel size using two-component columnar LC systems. A polymerizable fan-shaped molecule bearing a diol moiety at the focal point has been designed and synthesized. No liquid crystallinity is observed for the diol monomer alone. However, the diol monomer is miscible to an imidazolium ionic liquid, 1-butyl-3-methylimidazolium bromide, to form tetragonal columnar LC phases. Infrared spectroscopy indicates the formation of hydrogen bonding between the ionic liquids and diol moieties in the LC mixtures. These results suggest that the formation of hydrogen bonding between the diol moieties and the ionic liquids promotes nanosegregation between the hydrophilic and hydrophobic moieties, leading to the stabilization of the columnar phases. The intercolumnar distance of the columnar phases increases as increasing the mole fraction of the ionic liquids, corresponding to the enlargement of ionic liquid channels in the center of the columns. Columnar nanostructured membranes have been prepared by in situ photopolymerization of the columnar LC mixtures and subsequent removal of the ionic liquids organized in the center of the columns. Infrared spectroscopy and XRD measurements confirm that the columnar nanostructures are maintained after photopolymerization and removal of the ionic liquids. The channel sizes after the removal of ionic liquids are estimated to be more than 1.5 nm. The columnar nanostructured water-treatment membranes exhibit virus rejection values over 99.99% and higher water permeability compared to the membranes based on thermotropic ionic columnar and bicontinuous cubic liquid crystals. The virus rejection performances of the columnar nanostructured membranes are changed depending on the mixing ratios of the diol monomer and the ionic liquid.

Chapter 4. Ion-Conductive Smectic Liquid Crystals Exhibiting Reentrant Phase Transition

In this chapter, the unique reentrant phase transition behavior of ion-conductive smectic liquid crystals is presented. Nanostructured LC ion conductors have attracted attention as new electrolytes because the nanochannels act as efficient ion transport pathways. Nanostructured LC electrolytes for lithium-ion batteries have been developed using carbonate-based smectic liquid crystals. Switching of ionic conductivity using thermal LC-LC phase transitions has also been demonstrated. In this chapter, it is found that a newly designed cyclic carbonate-based molecule containing an alicyclic bicyclohexyl mesogen and a tetra(oxyethylene) spacer exhibits an unexpected reentrant phase transition. The intension in this chapter is to study the mechanisms of the unusual reentrant behavior in the layered LC assemblies and to achieve multistep changes in ionic conductivity using the reentrant LC phase transition. SmA phases typically appear at higher temperatures than SmB phases because SmA phases lack intralayer order, while SmB phases have intralayer hexatic order. However, the carbonate-based molecule exhibits reentrant LC phase transition; smectic A (SmA)-smectic B (SmB)-reentrant smectic A (SmA_{re}) on cooling. The assembled structures of the smectic phases are studied by XRD measurements, electron density profiles, and molecular dynamics simulations. In the SmA phase, the bicyclohexyl mesogens overlap and tetra(oxyethylene) chains are highly tilted or folded. In the SmB phase, both the bicyclohexyl mesogens and tetra(oxyethylene) chains overlap. In the SmA_{re} phase, tetra(oxyethylene) chains are elongated and overlapped, while the bicyclohexyl mesogens do not overlap but align in head-to-head orientation. In the transition from the SmB phase to the SmA_{re} phase, the intralayer hexatic order disappears due to the realignment of the bicyclohexyl mesogens to adjust their cross-section to the narrowed tetra(oxyethylene) chains. These results suggest that the reentrant LC phase transition is induced by competition between the packing of rigid bicyclohexyl mesogens and the stepwise conformational changes of flexible tetra(oxyethylene) chains with temperature. Analogous molecules with different mesogens have been synthesized and the influence of mesogenic groups on LC properties is described. The mixture of the cyclic carbonate-based reentrant liquid crystal and

lithium tetrafluoroborate in the 95:5 molar ratio maintains the reentrant LC behavior. Ionic conductivities of the LC mixture have been measured on cooling from isotropic liquid. A sudden increase in conductivity is observed at the transition to the SmA phase because of the formation of 2D ion transport pathways. On further cooling, the conductivity decreases at the transition to the SmB phase, which is attributed to the in-layer hexatic packing of molecules. Finally, the conductivity increases again at the transition to the SmA_{re} phase due to the collapse of the in-layer hexatic order. The potential of the material as stimuli-responsive LC electrolytes is suggested.

Chapter 5. Conclusion and Perspective

In the present thesis, the development of nanostructured materials with transport and separation functions, such as water-treatment membranes and ion conductors, using the precise nanochannels formed by LC self-assembly as transport pathways for water and ions is described. In chapter 1, general introductions for this study are described. In chapter 2, cross-linked 2D nanostructured water-treatment membranes have been developed based on gemini smectic LC monomers. The uniform 2D nanochannels contributed to efficient virus rejection and improved water permeability. In chapter 3, columnar nanostructured water-treatment membranes with larger nanochannels have been developed using two-component columnar liquid crystals. In chapter 4, ion-conductive smectic liquid crystals that exhibit a unique reentrant phase transition have been developed by competing with molecular packing and conformation. Multistep changes in ionic conductivities have been realized based on the observed reentrant LC phase transitions.

In conclusion, this thesis demonstrates new design guidelines for the development of molecular-based environmental and energy functional materials for sustainable societies. The results obtained in this thesis will provide new insights on the emergence of functions through molecular self-assembly.

List of Publications

Original Papers

[1] "Gemini Thermotropic Smectic Liquid Crystals for Two-Dimensional Nanostructured Water-Treatment Membranes" Kazuma Hamaguchi, Rino Ichikawa, Satoshi Kajiyama, Shotaro Torii, Yusuke Hayashi, Jiro Kumaki, Hiroyuki Katayama, Takashi Kato, *ACS Appl. Mater. Interfaces* **2021**, *13*, 20598-20605.

[2] "Nanostructured Virus Filtration Membranes Based on Two-Component Columnar Liquid Crystals" Kazuma Hamaguchi, Daniel Kuo, Miaomiao Liu, Takeshi Sakamoto, Masafumi Yoshio, Hiroyuki Katayama, Takashi Kato, *ACS Macro Lett.* **2019**, *8*, 24-30.

[3] "Reentrant 2D Nanostructured Liquid Crystals by Competition between Molecular Packing and Conformation: Potential Design for Multistep Switching of Ionic Conductivity" Kazuma Hamaguchi, Huanjun Lu, Shota Okamura, Satoshi Kajiyama, Junya Uchida, Shunsuke Sato, Go Watanabe, Yoshiki Ishii, Hitoshi Washizu, Goran Ungar, Takashi Kato, *ChemPhysChem* **2023**, *24*, e202200927.

[4] "Hydrogen-Bonded Structures of Water Molecules in Hydroxy-Functionalized Nanochannels of Columnar Liquid Crystalline Nanostructured Membranes Studied by Soft X-ray Emission Spectroscopy" Kazuma Hamaguchi, Takeshi Sakamoto, Naoya Kurahashi, Yoshihisa Harada, Takashi Kato, *J. Phys. Chem. Lett.* **2024**, *15*, 454-460.

Reference Papers

[1] "High Virus Removal by Self-Organized Nanostructured 2D Liquid-Crystalline Smectic Membranes for Water Treatment" Daniel Kuo, Miaomiao Liu, K. R. Sunil Kumar, Kazuma Hamaguchi, Kian Ping Gan, Takeshi Sakamoto, Takafumi Ogawa, Riki Kato, Nobuyoshi Miyamoto, Hiroki Nada, Masahiro Kimura, Masahiro Henmi, Hiroyuki Katayama, Takashi Kato, *Small* **2020**, *16*, 2001721.

[2] "Nanostructured Liquid-Crystalline Li-Ion Conductors with High Oxidation Resistance: Molecular Design Strategy towards Safe and High-Voltage-Operation Li-Ion Batteries" Atsushi Kuwabara, Mayu Enomoto, Eiji Hosono, Kazuma Hamaguchi, Taira Onuma, Satoshi Kajiyama, Takashi Kato, *Chem. Sci.* **2020**, *11*, 10631-10637.