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## 学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称    博士 (理学)    氏名   曹   思雨

### 学 位 論 文 題 名

Study on Electroactive Soft Actuators Based on Nanostructured Columnar Liquid-Crystalline Polymer Electrolytes  
(ナノ構造カラムナー液晶性高分子電解質に基づく電気活性ソフトアクチュエータに関する研究)

Ionic electroactive polymer (**iEAP**) actuators that show reversible mechanical deformation by ion migration in response to an electric field have received enormous interest in the fields of artificial muscles, soft robotics, and haptics. Polymer electrolytes are one of the essential components for achieving high performance in **iEAP** actuators. Conventionally, amorphous ion gels and hydrated ionic polymers have been employed as electrolytes. But, as the ions are transported by segmental motion of the polymer backbone or by diffusion in the entangled polymer chains, the ionic conductivities are in the range of  $10^{-4}$ – $10^{-7}$  S  $\text{cm}^{-1}$  at ambient temperature. A new efficient electrolyte design that can transport a large number of ions in a shorter distance is important to achieve fast and low-voltage-driven actuation. The author expected that the formation of continuous ionic channels into polymer electrolytes should lead to achieve fast response and large bending for **iEAP** actuators. Liquid-crystalline (**LC**) materials are one of the promising candidates for the preparation of nanostructured low dimensional ion-transporting channels. Up to now, a variety of liquid-crystalline electrolytes forming columnar and lamellar structures have been successfully applied in lithium-ion batteries and dye-sensitized solar cells. However, no **iEAP** actuators using ionic **LC** electrolytes have been developed. In this thesis, a new family of columnar **LC** polymer electrolytes forming 1D and 3D ion channels have been developed by two different self-assembly approaches and successfully applied in soft **iEAP** actuators for the first time.

In chapter 1, the general background of actuators including the working mechanism and recent development of **iEAP** actuators and ion-conductive **LC** materials are described. The objectives of this thesis are given.

In chapter 2, the author focused on the columnar **LC** derivatization of a zwitterionic molecule as a medium for proton transport. Imidazolium sulfobetaine is one of the zwitterions in which the charge-delocalized cation and anion are covalently bonded. The zwitterion tethering a fan-shaped polymerizable mesogen is expected to form 1D ionic channels, but have no transportable ions. After addition of protic salts, the salts may be dissociated by the interactions with the zwitterionic moiety, which allows ions to move along the ionic pathways. Nanostructured proton and lithium-ion conductors were previously developed by co-assembly of low-molecular weight **LC** zwitterions and acidic molecules or lithium salts. However, the preparation of anhydrous 1D proton transporting polymer materials is still challenging. In this chapter, the author developed a new family of proton-conductive free-standing polymer films with randomly oriented 1D nanochannels by the columnar **LC** self-assembly of protic ionic liquids (**IL**) and a photopolymerizable fan-shaped zwitterionic molecule and the subsequent interlocking of the structures by *in situ* photopolymerization. Selecting the ionic liquids as nonvolatile electrolytes is the key to inducing nanostructured **LC** phases. The combination of the zwitterionic monomer and imidazolium bis(trifluoromethylsulfonyl)imide in the presence of water provided the room-temperature columnar liquid crystals, whereas the zwitterionic mixture with 1-butyl-3-methylimidazolium hydrogen sulfate formed the thermotropic columnar liquid crystals at

room temperature without water. The polymer membranes obtained from the thermotropic columnar **LC** assemblies showed the anhydrous conductivities of  $10^{-6}$ – $10^{-9}$  S cm<sup>-1</sup> at room temperature. In contrast, the hydrous polymer membranes obtained from the lyotropic columnar **LC** assemblies exhibited higher ionic conductivity in the order of  $10^{-4}$ – $10^{-3}$  S cm<sup>-1</sup> at room temperature due to the accelerated ion diffusion by the incorporation of water molecules into the ionic channels. Furthermore, the hydrous columnar **LC** membranes showed 100–1000 times higher conductivity than the amorphous polymer films prepared by photo-preservation of the monomeric mixtures in the isotropic liquid state. The author has demonstrated that the nanostructured complexes of zwitterionic monomer and protic **ILs** can efficiently transport ions in the solid polymer matrices.

In chapter 3, the 1D nanostructured **LC** polymer film electrolytes were applied in **iEAP** actuators and their actuation performance was evaluated under various conditions. The columnar **LC** polymers with the thickness of 64 μm were sandwiched between two conducting polymer electrodes, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (**PEDOT:PSS**). The strip showed a bending motion to the anode side, probably due to the swelling of the cathode layer by the accumulation of larger size of cations on the cathode. The anhydrous actuators showed a maximum bending strain of 0.65% under an alternating current (AC) voltage of ±2 V at a frequency of 0.01 Hz under ambient conditions and generated 1.2 mN under a direct current voltage of 2 V for 2 min. On the other hand, the maximum value of bending strain of the hydrous polymer electrolytes reached 0.84% under an AC bias of ±2 V at 0.1 Hz in 70% RH. The bending strain and generated blocking force can be enhanced by increasing the ion content in the **LC** polymers and employing ionic liquids with large volume differences between cations and anions. It is found that the use of thicker **LC** electrolytes can enhance the blocking force but reduce the bending strain. In this chapter, the novel soft actuators based on the columnar **LC** polymer film electrolytes organizing protic **ILs** into the 1D nanochannels were developed to induce large bending strain and blocking force at low driving voltage.

The uniform alignment of the 1D channels in the direction perpendicular to the columnar **LC** electrolyte membranes is expected to improve the ionic conductivity and actuator performance. However, it is quite difficult to control the orientation in the thick films exceeding 50 μm. In chapter 4, the author aimed to develop a new type of ion-conductive liquid crystal/polymer composite electrolyte forming 3D continuous nanochannels as an alignment free electrolyte showing high ionic conductivity. A rod-like zwitterionic molecule containing an imidazolium sulfobetaine moiety was designed and synthesized because the interaction of zwitterionic moiety and ionic liquids may change the molecular shape from rod-like to conical, which is favorable for the induction of inverted columns. The self-assembly of the zwitterionic mesogenic compound, 1-butyl-3-methylimidazolium triflate as an ionic liquid, and poly(vinyl alcohol) (**PVA**) as a mechanically supported polymer matrix successfully induced a hexagonal columnar **LC** structure that formed 3D ionic transporting channels surrounding the mesogenic columns for the first time. These composite electrolytes maintained the columnar **LC** structures in humidified conditions over 60% RH and showed a mechanical stretchability. The actuator strips composed of the composite electrolyte and **PEDOT:PSS** exhibited a large displacement of 15 mm under the application of an AC voltage of ±1 V at 0.1 Hz in 70% RH. The bending strain reached 0.32%, which is larger than those of reported amorphous **iEAP** actuators containing larger amount of ionic liquids. In addition, the bending speed of **LC**/polymer composite actuator was two times faster than that of the amorphous actuator consisting of **PVA** and the same amount of ionic liquid under an AC bias of ±0.5 V. In this chapter, the author demonstrated that the inverted columnar **LC**/polymer composite films with 3D interconnected ionic channels can be a new soft actuator that exhibits fast and large deformation at low driving voltage despite the low ion content.

In chapter 5, overall summary of this thesis and future perspectives are presented. This thesis has reported columnar **LC** polymer films confining ionic liquids into 1D and 3D channels and the first application to electroactive actuators that exhibited low-voltage-driven bendability and force generation in the air and humidified conditions. This work has unveiled a direct correlation between the nanochannels and the actuation performances. The concept of **LC** nanosegregation may lead to new designs for **iEAP** actuators to achieve the conflicting functions of high-power generation and fast motion.