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Development of Intelligent Ion Exchange Membrane Controlled by External Stimuli

Masahiro Funahashi, Shinobu Uemura

Kagawa University

Summary

In conventional ion exchange membranes, ions are transported by electrostatic interaction between charged ions and ionic functional groups fixed on the polymer chains. Ion-transmittance is determined by the structure of the polymers and the transmittance cannot be controlled by eternal stimuli. Ion exchange membranes of which ion transmittance can be controlled by external signals caused by chemical substances or electrical stimuli should be effective to realize the efficient production process of salts. In this study, we synthesized liquid-crystalline perylene bisimide derivatives which can be applied to the ion exchange membranes of which ion transmittance can be controlled by the external stimuli.

Perylene bisimide derivatives bearing cyclotetrasiloxane rings and one triethylene oxide chain were synthesized. These compounds exhibit the columnar phases at room temperature. These compounds are soluble in organic solvents and liquid-crystalline thin films can be produced by a spin-coating method. In the thin films deposited on bare glass plates, columnar axes are parallel to the substrates. However, PVA film is deposited on the liquid-crystalline films and they are thermally treated, to produce thin films in which the columnar axes are aligned perpendicular to the substrates. These liquid-crystalline thin films are insolubilized via ring opening polymerization induced by the exposure on the acid vapors. These polymerized films indicate anisotropic ion transmittance.

Perylene bisimide derivatives bearing cyclotetrasiloxane rings as well as three triethylene oxide chains were also synthesized. These compounds exhibit the columnar phases at room temperature. For spin-coated thin films of these compounds, control of the columnar axes and the *in situ* polymerization induced by the acid vapors in the thin film states are possible. These polymerized thin films display the anisotropic electrochromism. For the thin films in which the columnar axes are aligned parallel to the substrates, ions do not permeate into the thin films and electrochromism is not observed under the application of the negative bias. In contrast, ions can permeate efficiently into the thin films in which the columnar axes are aligned perpendicular to the substrates and the thin films indicate electrochromism between red and blue.

For the purpose of the production of ion-selective films, perylene bisimide derivative bearing a crown ether moiety was synthesized. This compound exhibits a columnar phase at room temperature. The liquid-crystalline thin films can be produced by the spin-coating method and the thin films can be insolubilized by the acid-vapor-induced *in situ* polymerization.