In-situ polymerization of liquid crystalline semiconductors bearing cyclotetrasiloxane rings

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Conventional liquid crystalline (LC) molecules have linear alkyl side chains. For LC molecules consisting of incompatible segments, the competition between weak intermolecular interactions promote nanosegregation in electroactive LC systems. We have reported perylene tetracarboxylic bisimide (PTCBI) derivatives bearing oligosiloxane side chains. They exhbit columnar and lamellar phases at room temperature and high solubility in various organic solvents. ²⁻³

In this presentation, we report *in-situ* ring-openeing polymerization of LC semiconductors. Cyclotetrasiloxane moieties polymerize in the presence of acid catalyst. Perylene tetracarboxylic bisimide (PTCBI) derivative 1 bearing four cyclotetrasiloxane rings exhibits a columnar phase at room temperature and does not crystallize when it is cooled to -100 °C, in spite of the presence of the bulky cyclotetrasiloxane rings. ⁴ The electron mobility in the columnar phase at room temperature increases to 0.12 cm²/Vs, which is comparable to those of molecular crystals. Compound 1 is soluble in various organic solvents and thin films can be produced by a spin-coating method. The spin-coated films are insolubilized by the exposure on the vapor of trifluoromethane sulfonic acid. During the polymerization process, the molecular aggregation structures are maintained.

We synthesized ferroelectric LC phenylterthiophene derivatives comprised of an extended π -conjugated system which have hole transport property.⁵ Even the LC compound 2 bearing a bulky cyclotetrasiloxane ring exhibits smectic phases. They exhibit high spontaneous polarizations of $50 \sim 150$ nC/cm² as well as hole mobilities on the order of 10^{-4} cm²/Vs in the ferroelectric chiral smectic C* phase. Prior to the application of the DC bias, UV light illumination induces photocurrent in the reversed polarity without the external DC bias. The inversion of the polarity of the DC bias causes the inversion of the polarity of the photocurrent. This should be attributed to anomalous photovoltaic effect which is sometimes observed in ferroelectric ceramics.

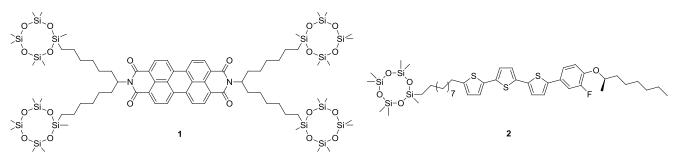


Fig. 1. Molecular structures of PTCBI derivatives bearing cyclic oligosiloxane moieties

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