

Elucidation of the Mechanism of the Solvent-Dependent Switch of Helical Main-Chain Chirality of Poly(quinoxaline-2,3-diyl)s in Alkanes by Small Angle Neutron Scattering

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Single-handed helical polymers have attracted much attention because of their applications for asymmetric catalysts, chiral stationary phase, and chiroptical materials. Recently, we developed the synthesis of helically chiral poly(quinoxaline-2,3-diyl)s (PQXs) bearing chiral side chains. Interestingly, PQXs exhibit solvent-dependent helix inversion, which can serve as effective scaffold for chirality-switchable polymer ligands and chiroptical materials. In order to reveal the mechanism of the solvent-dependent helix inversion of PQXs and control it, it is highly desirable to clarify the structural change of the PQXs before and after the solvent-dependent helix inversion.

In our previous report, we have suggested a hypothesis that conformational changes of the side chains caused by solvent effect induces the helix inversion of the PQX backbone. When the solvent could be incorporated into the side chain moiety, the side chains are extended and induce the right-handed helical conformation of the backbone. On the other hands, when the solvent could be excluded from the side chain, the side chains are shrunken and induce the left-handed helical conformation.

In this study, in order to prove this hypothesis, we focused on the temperature-dependent helix inversion of a PQX bearing (S)-3-octyloxymethyl side chains dissolved in n-octane-d18 to clarify the change of the side chain configuration by small angle neutron scattering (SANS). Before the SANS experiments, we have carried out circular dichroism (CD) measurements of

the PQX dissolved in n-octane at various temperature, which exhibited the helix inversion between 313 K and 333 K. The obtained SANS patterns of the PQX dissolved in n-octane-d18 at 313, 333, 353, and 373 K are shown in the figure. Now, we are trying to reveal the conformational changes of the chiral side chains of the PQX through molecular dynamics calculations.

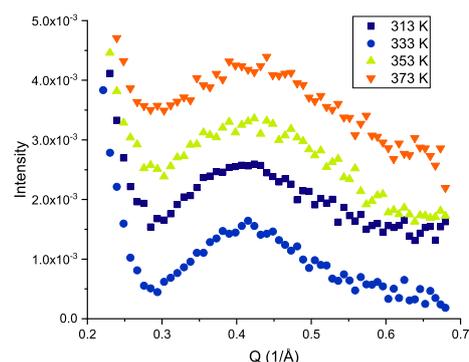


Fig. 1. SANS patterns of the PQX in n-octane-d18 at 313, 333, 353, and 373 K