QENS Studies of Fast Molecular Reorientation in Isotropic, Glass, Smectic, and Crystalline Phases of 6O2OCB

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Some of cyanobiphenyl compounds are well known as liquid crystalline materials. These molecules are rod-shaped consisting of two parts (rigid cyanobiphenyl part and flexible alkyl-chain part), which is one of the keys of forming a liquid crystalline phase. The phase behavior of liquid crystalline material is quite sensitive to a small change in molecular shape. Branching modification of the alkyl-chain for cyanobiphenyl compounds is one of such changes, which varies not only the behavior of liquid crystalline phases but also the crystalline polymorphisms. We have been interested in the relation between the phase behavior and alkyl-chain motion of such compounds. In the past two years, we reported the results of the quasi-elastic neutron scattering (QENS) measurement of (S)-4-(2-methylbutyl)-4-cyanobiphenyl (5*CB) and (S)-4-(1-methylheptyloxy)-4-cyanobiphenyl (8*OCB) both of which are the structural isomer of famous liquid crystalline materials 5CB and 8OCB having branching structure in their alkyl-chains. From those investigations, it has been revealed that the chain branching significantly slows down the motion of alkyl-chain as well as the rotational motion of whole molecule around its long axis. This year, we report the results of QENS measurement for another cyanobiphenyl compound 4-(2-hexyloxy-ethoxy)-4'-cyanobiphenyl (6O2OCB) which is analogous to 8OCB having ?OCCO? structure in its alkyl-chain.

Various kinds of measurements have already been made for 6O2OCB. From the calorimetric measurements, the phase behavior of 6O2OCB has been established [1]. The isotropic liquid is easily undercooled and forms glassy state on further cooling below 218 K. There exist two liquid crystalline phases (both of which are metastable smectic) and two crystalline phases (metastable and stable). The phase behavior of 6O2OCB is significantly different from that of 8OCB which has two liquid crystalline phases (nematic and smectic). The dielectric relaxation measurements have also been made, and they showed that the molecular reorientation around its short axis becomes quite slow near the glass transition temperature at 218 K [1]. The purpose of this experiment was to investigate the molecular reorientation around its long axis and the internal molecular motions.

We performed QENS experiments on 6O2OCB using AGNES spectrometer at JRR-3M. The measurements were made at 370 K, 350 K, 330 K, 310K, 290 K for isotropic liquid phase with a low-resolution mode (delta E = 120?micro-eV). As a spectrum of rotational motion is approximately described by sum of a delta function (an elastic component) and a Lorentz function (a quasielastic component), we first fitted the spectra with these two functions. However, the result was not quite. We next tried to fit the data with two Lorentz functions, which was actually better. The HWHM of the Lorentz function for narrow component increases with increasing momentum transfer (Q), indicating the narrow component as a diffusive motion. The diffusion constants were obtained by using the continuous diffusion model. An Arrhenius plot for the diffusion constant gives the activation energy 22.1 kJ /mol (Fig. 1). This motion may be the mixture of the alkyl-chain tumbling motion and the rotation of whole molecule around its long axis.

One of the interesting points is that the diffusion constant of 6O2OCB is smaller than that of 8OCB while it is larger than that of 8*OCB, which indicates that the ?OCCO? structure in its alkyl-chain slows down the chain motion less significantly than the chain-branching effect. Since 6O2OCB shows two liquid crystalline phases while no liquid crystalline phase is found for 8*OCB, there seems some correlation between the speed of alkyl-chain motion and the formation of liquid crystalline phase.

[1] Massalska-Arodz M., Sciesinska E., Sciesinski J., Krawczyk J., Inaba A., Zielinski P.M., Dielectric Properties of Liquid Crystals, eds Z. Galewski, L. Sobczyk (Research Signpost Publ.); ISBN: 978-81-7895-288-8 (2007) 160.

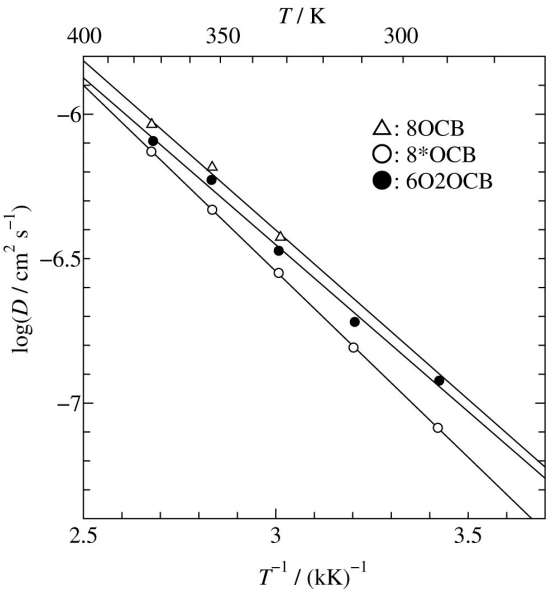

Fig. 1. Fig. 1 An Arrhenius plot of the diffusion constant for 6O2OCB, 8OCB and 8*OCB.