QENS studies of Fast Molecular Reorientation in Liquid, Glass and Crystalline Phases of 8*OCB

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Chain branching and chirality of molecules affect various physical properties substantially, such as phase behavior. Some of cyanobiphenyl compounds are good examples whose phase behavior varies depending on the presence of branch (chirality) in the alkyl side chain. We have been interested in their phase relation and dynamics. Here, we report the results obtained from quasielastic neutron scattering (QENS) measurements for (S)-4-(1-methylheptyloxy)-4-cyanobiphenyl (8*OCB) which is one of such cyanobiphenyl compounds.

Various kinds of measurements have already been made for 8*OCB. From the calorimetric measurements [1] and IR spectroscopy [2], the phase behavior of 8*OCB was established. The isotropic liquid is easily undercooled and forms glassy state on further cooling below 218 K. There exist two crystalline phase (metastable and stable). This phase behavior is entirely different from that of the non-chiral isomer, 8OCB, which has two liquid crystal phases (nematic and smectic). The dielectric relaxation measurements [3] 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. 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 8*OCB using AGNES spectrometer at JRR-3M. The measurements were made at 370 K, 350 K, 330 K, 310K, 290 K, 270 K for isotropic liquid phase with a low-resolution mode (delta E = 120?micro-eV). As a reference sample, 8OCB was also investigated at 370 K (isotropic liquid), 350 K (nematic), 330 K (smectic) and 310 K (crystal).

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 23.5 kJ /mol (Fig. 1). The 8OCB spectra could also be fitted by two Lorentz functions. The HWHM of the narrow component was significantly broader than that of 8*OCB, which means that this diffusive motion of 8OCB is faster than that of 8*OCB. However, the diffusion constants of 8OCB determined in this QENS experiment were clearly larger than those obtained before by NMR measurements [4] (Fig. 1). In addition, rotational diffusion constants about its long axis for 8OCB, obtained by another NMR measurements [5], are about 10 nsˆ-1 at 340 K. This value is in the resolution-window of AGNES, so we must have observed this motion. Therefore, the narrow component should be interpreted as a coupled motion of translational diffusive motion and rotation around its long axis.

For the broad component, the activation energy was determined to be 4.8 kJ/mol by an Arrhenius plot of the HWHM. This motion may be some internal molecular motion such as rotation of the methyl groups

or tumbling motion of the alkyl chain. The rotational diffusion coefficient was estimated to be around 1.2 rad/ps at 350 K. For this broad component, the results of 8*OCB and 8OCB are almost same. It should be added that this motion was observed in the crystalline phase of 8OCB at 310 K as well, while it was not observed in the metastable or the stable crystal for 8*OCB at 270 K.

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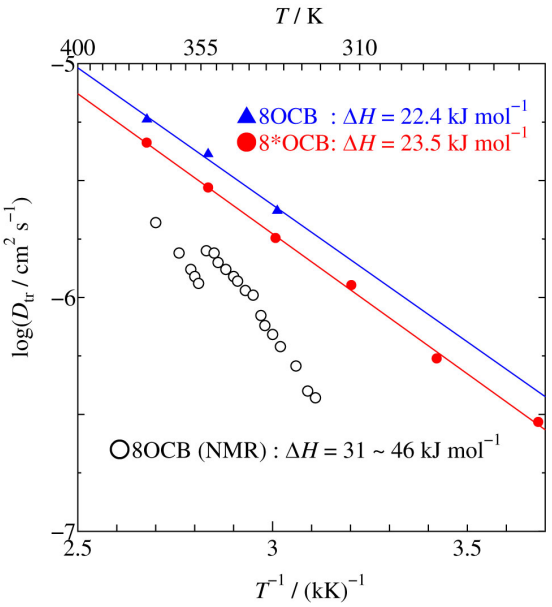

Fig. 1. Fig. 1 An Arrhenius plot of the diffusion constant for 8*OCB and 8OCB obtained in this QENS study, and the translational diffusion constant for 8OCB obtained by NMR measurements (Ref. 4).