Dynamics of super-high entropy liquids alkylated tetraphenylporphyrins

O. Yamamuro(A), M. Nirei(A), M. Kofu(B), T. Nakanishi(C), G. Avijit(C), M. Tyagi(D)(E)
(A)ISSP-NSL Univ. Tokyo, (B)J-PARC, (C)NIMS, (D)NIST, (E)Univ. Maryland

Recently, Nakanishi group in NIMS found that large molecules, 3,5-C6C10-tetraphenylporphyrin and 2,5-C6C10-tetraphenylporphyrin, exist in liquid states at room temperature. Taking account of the fact that tetraphenylporphyrin (TPP) has a melting temperature of 723 K, the liquid phases of alkylated TPP should be stabilized by the large entropy effect which is caused by the conformational disorder of long alkylchains. This situation is similar to that of ionic liquids which are in liquid states in spite of their strong inter-ionic interactions. We call this type of liquids "super-high entropy liquids".

The purpose of this work is to clarify the dynamical feature of the alkylchains in 3,5-C6C10-TPP and 2,5-C6C10-TPP by means of QENS. This method can effectively observe the motions of alkylchains with many hydrogen atoms. Following the work on AMATERAS at J-PARC (energy resolution: 0.01-1 meV), we have carried out the QENS experiment on HFBS (energy resolution: 0.8 micro-eV) at NIST. The QENS measurements were carried out at 200, 220, 240, 260, 280, 300, 325, 350, 375 and 400 K on both spectrometers. We have combined the I(Q,t) data, which are the Fourier transformation of the S(Q,E) data, obtained by the two spectrometers. Then, the I(Q,t) data were fitted to the two KWW functions corresponding to the relaxations of alkylchains and a whole molecule (alpha-relaxation). The non-exponential parameter beta is a fitting parameter for the alkyl relaxation and fixed to be 0.5 for the alpha relaxation.

Figure 1 shows the Arrhenius plot of the averaged relaxation times and beta values. The alpha-relaxation of 2,5-C6C10-TPP is faster than that of 3,5-C6C10-TPP. This may be related to the fact that the viscosity of 3,5-C6C10-TPP (75 Pa s at 298 K) is ca. 5 times larger than that of 2,5-C6C10-TPP (16 Pa s at 298 K). On the other hand, the relaxations of alkylchains are almost the same. And the alpha-relaxation time seems to diverge at the glass transition temperature, but that of alkylchains seems to be linear and independent of the alpha-relaxation. From the Q-dependence of relaxation time, we have found that the alkylchain motion is diffusion in a confined space of ca. 0.6 nm, while the alpha-relaxation is continuous diffusion.

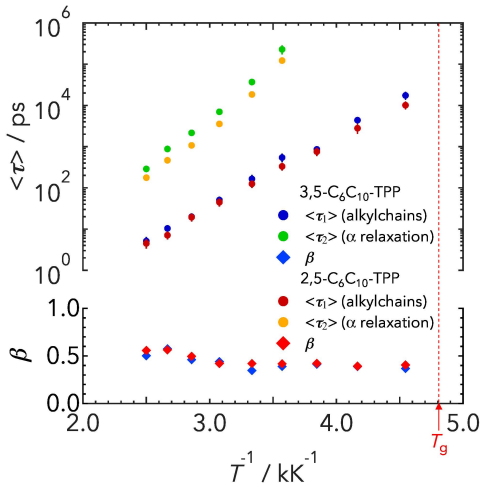

Fig. 1. Arrhenius plot of averaged relaxation times and beta values for alkyl relaxation.