Dynamics of super-high entropy liquids alkylated perfluorobenzenes

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The fusion (melting) temperature T_{fus} of molecules usually depend on molecular mass M; the larger M is, the higher T_{fus} becomes. For example, T_{fus} of benzene (C_6H_6, M = 78) is 279 K while that of biphenyl (C_6H_5-C_6H_5, M = 154) is 342 K. This is because the intermolecular van der Waals interaction is larger in the crystalline phase with denser molecular packing than that in the liquid phase with coarser packing. Recently, Nakanishi group in NIMS found that large molecules, 2,5-C_6C_{10}-tetraphenylporphyrin (2,5-C_6C_{10}-TPP) [1] and C_8C_{12}-perfluoro-benzene (C_8C_{12}-PFB), exist in liquid states at room temperature. It is quite interesting that T_{fus} of these alkylated molecules (2,5-C_6C_{10}-TPP, M = 2538; C_8C_{12}-PFB, M = 465) is lower than T_{fus} of non-alkylated molecules (TPP, M = 615, T_{fus} = 723 K; PFB, M = 186, T_{fus} = 278 K). We consider that these alkylated molecules are 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 interionic interactions. We collectively call this type of liquids "super-high entropy liquids (SHEL)".

In the present experiments, we have measured quasielastic neutron scattering (QENS) of alkylated perfluorobenzenes (APFB). These molecules are much smaller and simpler than alkylated TPP (ATPP), whose QENS have already been measured by us. The purpose of this work is to investigate the common dynamical features in APFB and ATPP. We take C_4C_8-PFB, C_6C_{10}-PFB and C_8C_{12}-PFB also to investigate the effect of the length of alkylchains.

Two QENS spectrometers, HFBS at NIST and TOFTOF at FRM II were used. They have different energy resolutions and can measure motions in different time regions (HFBS: 100 ps -10 ns, TOFTOF: 0.5 ps - 100 ps). To observe temperature dependence of motion, QENS have been measured at 4 or 5 temperature points above the glass transition temperature of each sample. $S(Q,\omega)$ data obtained by HFBS and TOFTOF were Fourier transformed to $I(Q,t)$ and then connected. $I(Q,t)$ curves were fitted to the two KWW functions corresponding to the relaxations of alkyl chains and the α-relaxations.

Figure 1 shows temperature dependence of $I(Q,t)$ curves of C_4C_8-PFB at Q = 1.0 Å^{-1} and fitting curves by two KWW functions. The fittings were satisfactory for all temperatures. The relaxation time of the α-relaxation tends to diverge at T_g, while that of alkyl chains is linear and independent of the α-relaxation. These results of APFB are quite similar to those of ATPP.

[1] A. Ghosh et al., Nat. Commun. 10, 4210 (2019).

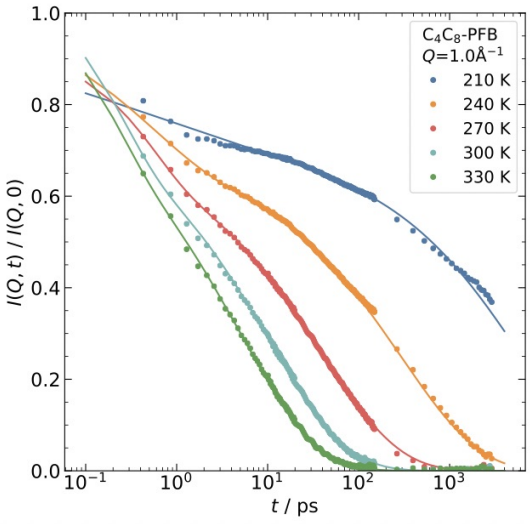

Fig. 1. Temperature dependence of $I(Q,t)$ of C_4C_8-PFB at Q = 1.0 Å^{-1} (circle) and fitting curves by two KWW functions (solid line).