

Quasielastic Neutron Scattering Study on Guest Molecules in Syndiotactic Polystyrene Co-crystals

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Syndiotactic polystyrene (sPS) exhibits a variety of solid states. One of the important characteristics of sPS is the formation of cocrystals, where organic compounds are stored as guests in the cavities in the crystalline region. It has been clarified that a wide variety of chemical compounds including functional molecules such as fluorescent and dye molecules can be stored as guest molecules. It has been clarified that the orientation and conformation of the guest molecules are strongly restricted by the field of the host lattice. So, it seems very likely that the host sPS lattice exerts a strong influence also over the dynamics of the guest molecule. Nevertheless, only few studies have addressed this question. The concrete information about the dynamics of the guest molecules based on empirical data is too scarce to draw a general picture of how guest molecules behave in the cage of a polymeric material. In order to fill this gap, we have tried to carry out high-resolution quasielastic neutron scattering (QNS) experiments concerning guest dynamics.

In order to avoid the strong incoherent scattering of sPS matrix, fully deuterated sPS (d-sPS) was synthesized. Benzene and p-xylene were used as guests. All the methyl proton atoms were substituted with deuterium atoms for guest p-xylene (d6-p-xylene). Quasielastic neutron scattering measurements were carried out in the temperature range between 5 and 320K using TOFTOF spectrometer installed at FRM II in Garching, Germany.

It has been found that there are significant differences in QNS spectra between guest molecules stored in the cavities in the crystalline region of deuterated sPS cocrystals, depending on the shape of guest molecules (Fig. 1). The

intensity of quasielastic components of d-sPS/benzene cocrystal is much larger than those of d-sPS/d6-p-xylene cocrystal. The disparity is significant beyond the difference in the number of hydrogen atoms per molecules (six for benzene and four for d6-p-xylene). Furthermore, the Q-dependence of quasielastic components is also more pronounced in d-sPS/benzene cocrystal. Since all methyl hydrogen atoms are substituted with deuterium atoms in d6-p-xylene, these differences are attributable to the motions of phenyl ring, suggesting the highly restricted motion of p-xylene in the cavity of sPS crystal lattice. Considering the shape of the cavity of sPS/p-xylene, a flattened oval elongated in one direction, it is expected that the phenyl ring of p-xylene carries out only a precessional motion along the long molecular axis connecting two methyl groups. On the other hand, benzene can be considered to perform two kinds of motions, one is the rotational diffusion around the six-fold axis and the other is the precessional motion of phenyl ring. These dynamical characteristics of benzene and d6-p-xylene molecules would give rise to the striking difference in quasielastic components.

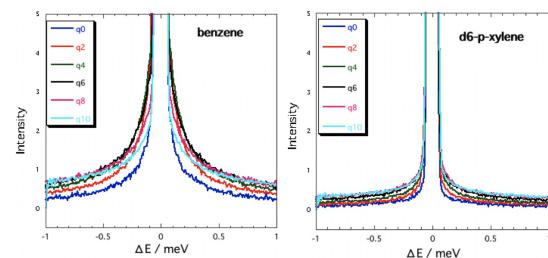


Fig. 1. QNS spectra of d-sPS/benzene and d-sPS/d6-p-xylene cocrystals measured at 320K with the Q range of 0.15-1.80Å⁻¹.