

# Dynamical Properties of Nanoporous Structure in Syndiotactic Polystyrene

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Syndiotactic polystyrene (sPS) is a relatively new commodity polymer, which exhibits a variety of crystalline states. The  $\delta_e$  phase of sPS occupies a unique position from the viewpoints of structure chemistry of polymers. In the  $\delta_e$  phase, there exist two relatively large cavities between sPS helices taking TTGG conformation. Each cavity has a volume of nearly  $120\text{\AA}^3$ . This nanoporous structure is regarded as the first example of molecular sieve in polymeric materials. Unlike the ordinary crystalline states of polymers, the density of the  $\delta_e$  phase ( $0.977\text{ g cm}^{-3}$ ) is less than that of the amorphous state ( $1.05\text{ g cm}^{-3}$ ). It seems that this unique structure exerts a considerable influence on the dynamical properties of the  $\delta_e$  phase.

In this study, we compared the QNS spectrum of the  $\delta_e$  phase with that of the  $\gamma$  phase and the glass state of sPS. In the  $\gamma$  phase, sPS helices take TTGG conformation like those of the  $\delta_e$  phase but they are much more densely packed. All QNS spectra were measured with AGNES spectrometer of JRR3M (Tokai). The mean-square displacement  $\langle u^2 \rangle$  of hydrogen atoms was evaluated from the  $Q$  dependence of the elastic scattering intensity  $I(Q)$  by using the following the Debye-Waller formula:  $I(Q) = I(0) \exp[-(1/3)\langle u^2 \rangle Q^2]$ , where  $I(0)$  is the elastic intensity at  $Q = 0$ . In order to reduce the effect of coherent scattering,  $I(Q)$  was divided by that at 20K.

Figure 1 shows the temperature dependence of  $\langle u^2 \rangle$  for the  $\delta_e$ ,  $\gamma$  and glass samples. The mean square displacement of the glass sample is larger than that of the  $\gamma$  and  $\delta_e$  phases in the whole temperature range of 100-350K. Although there is no conspicuous difference in  $\langle u^2 \rangle$  between the two crystalline phases,  $\delta_e$  and  $\gamma$ , up to 250K, the  $\delta_e$  phase shows a clearly

larger displacement in the higher temperature region, which is attributable to the weaker interchain interaction in  $\delta_e$  phase. As for the QNS component, these samples exhibit their own characteristics; the  $\delta_e$  phase shows a larger contribution to the high  $Q$  and low  $\Delta E$  region, suggesting the activation of local motions.

According to the previous  $^{13}\text{C}$ -NMR study by Gomez and Tonelli, the spin-lattice relaxation times  $T_1$  are shorter in the  $\delta_e$  phase than the glass. We conjecture that the difference in the NMR and QNS experiments is due to the time scale of detectable molecular motion. Considering all the various factors together, we infer that the influence of the nanoporous structure appears most conspicuously in slow and large motions. However, we can see from the results of QNS that smaller molecular motions of shorter time scale, which are probably the phenyl group's motions, are more activated in the nanoporous  $\delta_e$  phase. To clarify the more detailed dynamical properties of the  $\delta_e$  phase, it is necessary to study the larger molecular motion of longer time scale.

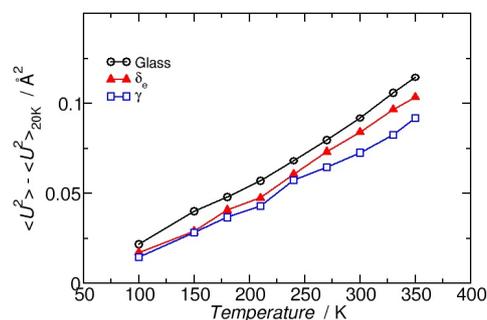


Fig. 1. Temperature dependence of mean square displacement in sPS solid states