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Structural Evolution in the Processes of Solvent-Induced Crystallization and Solvent Exchange Phenomena Observed for syndiotactic Polystyrene

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Syndiotactic Polystyrene (sPS) is known to crystallize when the glassy sample is exposed in an atmosphere of such solvent as toluene or chloroform. The thus-created crystal is a complex of sPS helical chains surrounded by solvent molecules. When a different type of solvent is supplied to this complex, an exchange between original and new solvents occurs quite easily. In a series of papers we have investigated the structural evolution processes in these phenomena from the molecular level on the basis of X-ray and infrared/Raman spectral data [*Macromolecules*, **36**, 3593 (2003)]. In order to clarify the changes in higher-order structure during these phenomena, we have performed the time-resolved measurements of wide- (WAXS) and small-angle X-ray scatterings (SAXS) in the beamlines of 10C and 15A of PF at KEK.

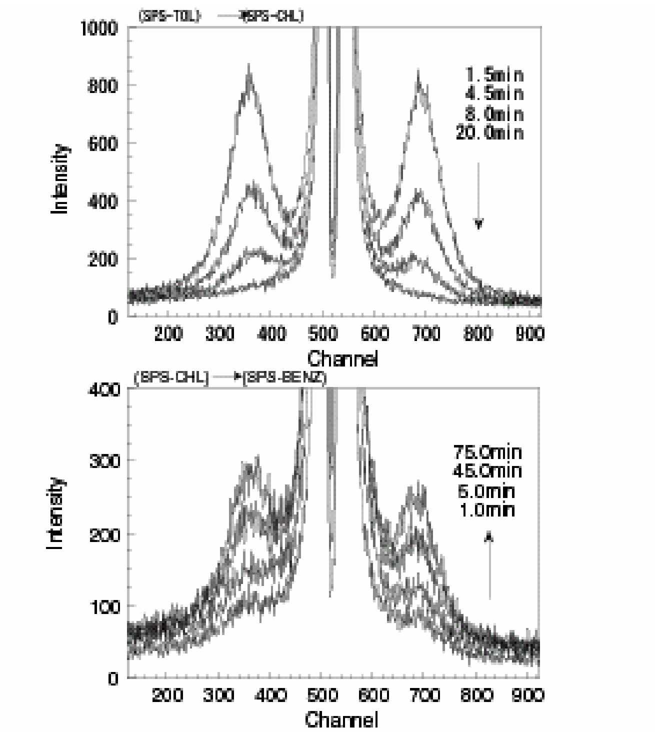

Figure 1. Time dependence of SAXS profile of sPS-solvent complex in the exchange process (a) from toluene to chloroform and (b) from chloroform. to benzene.

Figure 1 shows the time dependence of SAXS profile measured in the solvent exchange process. The SAXS pattern of oriented sPS-toluene complex shows a clear peak corresponding to the long period of ca. 100 Å. When chloroform was supplied to this sample, the SAXS intensity decreased rapidly due to the X-ray absorption effect by chlorine atoms. But, the peak intensity was recovered when benzene was supplied to sPS-chloroform system. In this way, the SAXS (and WAXS) pattern has been found to change rapidly in the solvent exchange process. Figure 2 shows the time dependence of SAXS intensity estimated for these processes. From these data it was found that the solvent exchange rate is in the order of chloroform > benzene > toluene. This is parallel to the order of crystallization rate: chloroform > benzene > toluene. The diffusion rate of solvent molecules and the interaction between sPS and solvent are considered to govern these rates, as reported in the previous papers.

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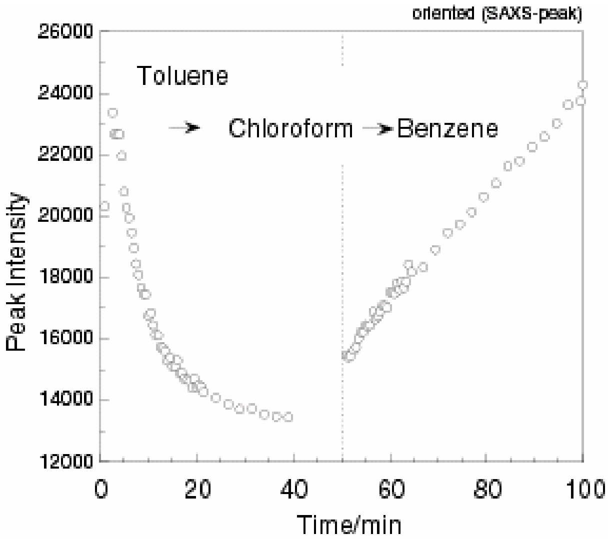

Figure 2. Time dependence of SAXS intensity measured in the solvent exchange process of sPS.