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Polymorphism of syndiotactic polystyrene from the molten state observed by the simultaneous DSC-XRD

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Introduction

Syndiotactic polystyrene (SPS) shows four polymorphisms, two crystalline forms containing molecular chains in TTTT conformation and two in TTGG conformation designated α, β, γ and δ, respectively. The former conformation is formed in the bulk polymerization. In this study, the crystallization process of SPS from the molten state was investigated by the simultaneous DSC-XRD measurement.

Experimental

SPS (Mn=17 x 10^4, Mw/Mn=2.3) used in this study was kindly supplied from Asahi Chemical Industry Co. Ltd. The amorphous press film was obtained by quenching from the molten state at 573 K. The amorphous SPS showed glass transition at 373 K, cold-crystallization at 419 K and melting at 548 K observed at 5 K/min. The DSC-XRD instrument was setting on SAXS optics at BL-10C, PF, KEK. The wavelength of X-ray was 0.1488 nm monochromated by double Si crystals. The size of X-ray was 0.6 x 0.6 mm.

After melting at 573 K for 5 mins, SPS was cooled to 473 K at various scanning rate from 1 K/min to 10 K/min. SPS was heated again to 573 K at 5 K/min immediately after arrived at 473 K. The time resolution of a XRD profile was 30 sec.

Results and discussion

Upon cooling a monotropic exothermic peak was observed on DSC curve in the temperature range from 515 K to 530 K depending on the cooling rate. However, two kinds of XRD diffraction peak at 0.7 nm^{-1} and 0.76 nm^{-1} were observed at the same temperature region. These XRD peaks were assigned to β(020) and α(110), respectively. On the other hand, two endothermic peaks sue to the melting were observed at 535 and 546 K on heating. The rate of both endothermic peak areas was influenced by the cooling rate. With increasing the cooling rate, the area of endothermic peak at 535 K and the XRD peak intensity of β(020) increased.

The DSC-XRD results for SPS cooled at 10 K/min and 2.5 K/min are shown in Fig.1 and 2, respectively. The temperature changes of XRD peak intensity of β(020) and α(110) are also plotted in figures. On Crystallization, the XRD peak of β(020) appears slightly faster than the XRD peak of a(110). However, both crystal forms grow at the same time on cooling. On heating, the XRD peak of β(020) started to decrease at the endothermic peak of the lower temperature and then the XRD peak at a(110) started to decrease at the higher endothermic peak. This result suggests that the endothermic peak at 535 K is due to the melting of b-form. However, the XRD peak of b(020) remains until the higher endothermic peak temperature. The crystal form obtained was determined not only by thermodynamic stability but also by kinetic process of crystallization.

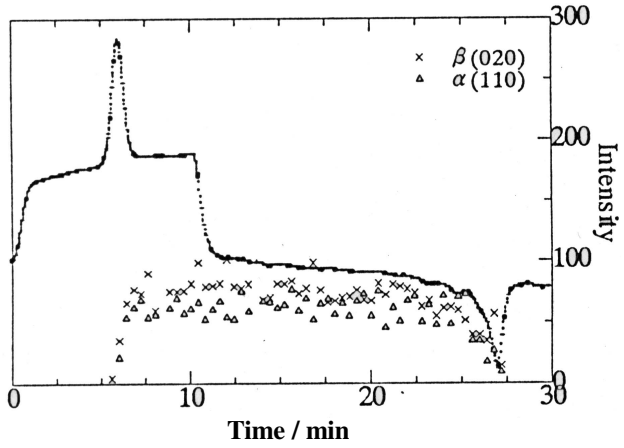

Fig.1 The DSC-XRD results of SPS obtained by cooling at 10 K/min and heating at 5 K/min

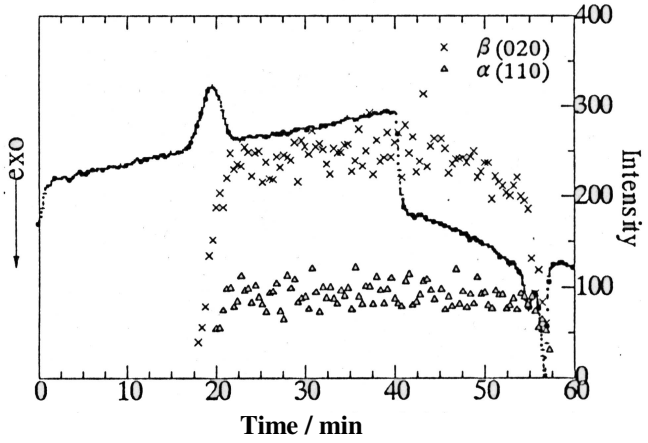

Fig.2 The DSC-XRD results of SPS obtained by cooling at 2.5 K/min and heating at 5 K/min

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