

Study on crystallization in novel gas barrier polymer

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Introduction

Gas barrier polymers with low gas permeability are used in order to protect contents from various gases in food packaging, fuel tank of automobile, protective coat of electronic products and so on. There are various gas barrier polymers for example, polyamide, poly(vinyl chloride) and ethylene-vinyl alcohol copolymer (EVOH). In particular among them, EVOH has excellent gas barrier property and oxygen permeability of EVOH is about three orders of magnitude smaller than that of polystyrene. It is widely used to various applications.

Recently, the novel polymers that have both stable gas barrier property independent of humidity and less permeability than EVOH have been tried to develop. In this report, one of such a gas barrier polymers was studied. The polymer is called high gas barrier polymer (HBP) in this study. The primary structure of HBP is similar to that of EVOH except that HBP is homo polymer and hydroxyl groups are placed periodically. Gas barrier property of HBP is more excellent and humidity dependence of permeability is lower than that of EVOH. However, the gas barrier property of HBP depends on condition of thermal treatment. Melt-crystallized (M-)HBP shows much lower permeability than EVOH while cold-crystallized (C-)HBP shows similar gas permeability to EVOH. According to the Bondi method [1], the free volume of M-HBP, C-HBP and EVOH are the same because they have same atomic groups. However, only the M-HBP showed much lower permeability. It is critically interesting phenomenon. The aim of this study is to clarify the reason why gas permeability of HBP changes by different condition of thermal treatment.

Experimental

The time dependence of long period during crystallization in HBP was investigated by small-angle X-ray scattering (BL-10C) at Photon Factory in KEK. The position sensitive proportional counter (PSPC) was used as a detector. The scattering profile was recorded per 30 seconds at a constant temperature. A detail of the SAXS has been described elsewhere [2].

Results and Discussion

Crystal structure and morphology of M- and C-HBP were measured by a differential scanning calorimeter (DSC) and wide-angle X-ray diffraction. It was found that both degree of crystallinity and crystal structure were almost the same between two samples. However, the morphology of two samples observed by a polarized optical microscope and a transmission electron microscope was vastly different. M-HBP had about 600 nm periodic co-continuous structure, whereas C-HBP did

not have significant structure. This difference may be generated by difference between the rate of crystallization and phase separation. In order to examine whether the crystallization or the phase separation happens early, a time resolved synchrotron SAXS profile in M-HBP was measured at 136°C (Figure 1). It was observed that the scattering intensity increased from 22min to 120min and finally the scattering peak was observed. From this result and those of light scattering measurement and DSC measurement, liquid-liquid phase separation occurred before crystallization and during induction period of crystallization in M-HBP. It was that M-HBP forms two different phases that were primary phase and secondary phase with different size of free volume. The reason why the phase separation occurs during induction period of crystallization is not clear at present, but it seems to be related to the arrangement of hydrogen bonds in amorphous region due to the periodic existence of -OH in polymer chain. Anyway, it was shown that this morphology concerned with gas barrier property.

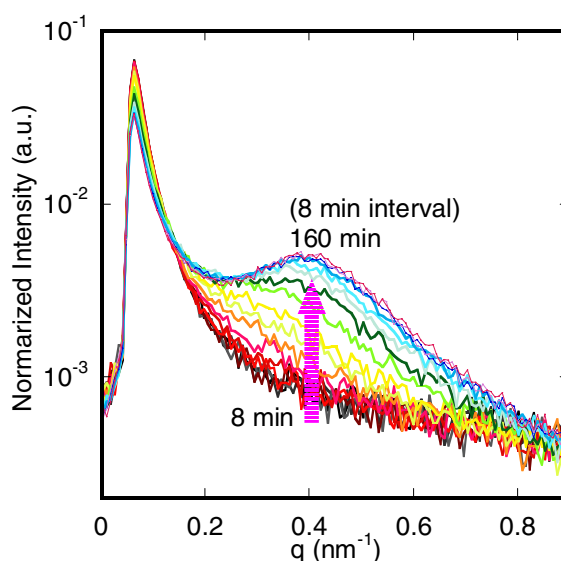


Figure 1. Change of synchrotron SAXS profile of HBP during melt crystallization at 136°C.

References

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