Structural Evolution in the Isothermal Crystallization Process of the Molten Nylon 10/10 Traced by Time-Resolved Infrared Spectral Measurements and Synchrotron SAXS/WAXD Measurements

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Abstract. The structural evolution in the isothermal crystallization process of nylon 10/10 from the melt has been clarified concretely on the basis of the time-resolved infrared spectral measurement as well as the synchrotron wide-angle and small-angle X-ray scattering measurements. Immediately after the temperature jump from the melt to the crystallization point, the isolated domains consisting of the hydrogen-bonded random coils were formed in the melt, as revealed by Guinier plot of SAXS data and the infrared spectral data. With the passage of time these domains approached each other with stronger correlation as analyzed by Debye-Bueche equation. These domains transformed finally to the stacked crystalline lamellae, in which the conformationally-regularized methylene segments of the CO sides were connected each other by stronger intermolecular hydrogen bonds to form the crystal lattice.

1. Introduction

Aliphatic nylon consists of the amide groups giving strong intermolecular hydrogen bonds and the methylene segments giving the flexibility to the skeletal chain. A sensitive balance between these two factors affects the hierarchical structure and physical properties of nylon. In other words, it is needed to clarify the formation process of the hierarchical structure to control the physical properties of this polymer by taking these two important factors into consideration. In a long history of nylon, however, there had been reported almost no paper describing the structural changes during the crystallization process from the melt. In the present study we have revealed successfully and in a concrete manner the structural evolution process of nylon 10/10, as one of the most typical aliphatic NYLONs, in the isothermal crystallization process from the melt by performing the time-resolved measurements of infrared spectra (FTIR) and synchrotron wide-angle X-ray diffraction (WAXD)/small-angle X-ray scattering (SAXS) patterns.
2. Experimental

The isothermal crystallization experiments have been performed by changing the temperature of the sample rapidly (ca. 1000°C/min) from above the melting point to the predetermined crystallization point. During this temperature jump, the time-resolved measurements of FTIR, WAXD and SAXS were carried out at a constant time interval (every 1 – 2 sec). The simultaneous measurements of WAXD and SAXS were performed using synchrotron X-ray source in the beam line BL40B2 of SPring-8, Japan. The samples used in the experiments were nylon 10/10 \{-[\text{NH}(\text{CH}_2)_{10}\text{NHCO}(\text{CH}_2)_{8}\text{CO-}]\} and nylon 10/10-d_{16} \{-[\text{NH}(\text{CH}_2)_{10}\text{NHCO}(\text{CD}_2)_{8}\text{CO-}]\}. The latter or partially-deuterated sample was useful especially in the infrared spectroscopic experiment since the infrared bands of methylene segments of the CO side were distinguished from those of NH side. The transition behaviours of these two samples were essentially the same each other.

3. Results and Discussion

3.1 Time Dependence of Infrared Spectra

Figure 1 shows the time dependence of infrared spectra measured in the frequency region of 3600 – 2800 cm\(^{-1}\) measured for nylon 10/10-d_{16} in the isothermal crystallization at 176°C.

![Figure 1. Time dependence of infrared spectra in the frequency region of 3600 – 2800 cm\(^{-1}\) measured for nylon 10/10-d_{16} in the isothermal crystallization at 176°C.](image)

In the melt before the temperature jump, the NH stretching band of the free hydrogen bonds \(\nu(\text{NH, free})\) was detected clearly at 3430 cm\(^{-1}\). At the same time, the \(\nu(\text{NH})\) band corresponding to the hydrogen-bonded amide groups (3300 cm\(^{-1}\)) was also detected, though it was rather broad in the melt. In this way, the intermolecular hydrogen bonds are existent still in the melt. This is a key point to understand the crystallization behaviour of nylon 10/10 as will be discussed in a later section. These hydrogen
bonds became stronger and their relative amount increased drastically immediately after the temperature jump. On the way of crystallization in a time region from 10 to 60 sec the hydrogen bonds were stabilized for a while (a plateau region observed for NH stretching bands in Figure 2). After that they started to become stronger furthermore, just when the methylene segments of the CO side were regularized in conformation. The methylene segments of the NH side were still in the disordered state [1].

3.2 Time Dependence of WAXD and SAXS Profiles

Figure 3 shows the time dependence of WAXD and SAXS profile in the isothermal crystallization process of nylon 10/10 at 176°C. For the quantitative analysis of SAXS data in the time region of 0 – 60 sec, we assumed that (i) in the earliest stage the locally-formed weak hydrogen bonds in the melt might cause the generation of some domains with relatively high density. These domains are isolated each other. (ii) As the time passes, these domains may transform to the stacked lamellae with relatively strong correlation. Then we analyzed the SAXS data on the basis of Guinier (for isolated domains; scattering vector $q < 0.007 \, \text{Å}^{-1}$) and Debye-Bueche theories (for correlated domains; $q > 0.007 \, \text{Å}^{-1}$) as well as the correlation function concerning the stacked lamellar structure.
As shown in Figure 4 (a), the Guinier plot \([\ln(I) vs \ q^2]\) gave the size of domain (or radius of gyration \(R_g\)) consisting of relatively strongly hydrogen-bonded coils [2]. As shown in Figure 4 (b) the Debye-Bueche plot \([\ I^{1/2} vs \ q^2]\) gave the averaged distance \(\xi\) (correlation length) between these domains [3]. Figure 5 shows the time dependence of the thus estimated \(R_g\) and \(\xi\) values. Figure 6 illustrates the relation between \(R_g\), \(\xi\) (and long period) given in Figure 5. As mentioned above, the \(R_g\) is the size of domain with almost no correlation with the neighboring domains. Once the crystallization is started, these domains approach more closely to each other due to the thermal contraction of the whole system, and at the same time the inner structure becomes more regular due to the increasing strength of hydrogen bonds, as revealed by the infrared spectral data. Once the correlation length, a measure of distance between the correlated neighboring domains, is close to the \(R_g\) [see Figure 6 (b)], the correlation between these regular parts start to increase. The correlation becomes stronger and approaches finally to the long period of the stacked lamellae. (It is noticed that the \(R_g\) was almost constant during this process as long as the Guinier plot was assumed to be applicable even for such a
weakly correlated domain structure as an approximation.) As the time passed beyond 60 sec, the $\xi$ value started to deviate from the linear straight line and transformed to the long period of stacked lamellae, about 240 Å. The SAXS data in this time region was analyzed by calculating the correlation function for the stacked lamellar structure [4], and the invariant $Q$ was estimated as seen in Figure 5.

### 3.3 Structural Evolution Process of Nylon 10/10

From Figure 5, we may draw the structural evolution process of nylon 10/10 in the isothermal crystallization from the melt as illustrated in Figure 7. At the earliest stage of crystallization from the melt, the intermolecular hydrogen bonds become stronger steeply and the amide groups of free hydrogen bonds decrease in population. These hydrogen bonds induce the local creation of isolated domains of relatively high density. As the time passes furthermore, these domains approach each other because the sample contracts gradually in the solidification process, during which the intermolecular hydrogen bonds are stabilized temporarily (10 – 60 sec region). After that the domains gather together more closely to form the stacked lamellar structure, in which the conformationally regularized methylene segments (the methylene segments of the CO side, strictly speaking) are packed in parallel and linked together by the strong intermolecular hydrogen bonds to form the crystal lattices.

(According to the infrared spectra measured for the partially-deuterated nylon 10/10 sample, the methylene segments of the NH side are still in the conformationally-disordered state even when the methylene segments of the CO side are already regularized. The reason for the difference in conformational regularization between these two kinds of methylene segments is not solved yet [1].)

![Figure 5. Time dependence of $R_g$ and $\xi$ compared with the infrared band data taken for nylon 10/10 in the isothermal crystallization at 176°C.](image)

![Figure 6. Schematic illustration of relationship between $R_g$, $\xi$ and long period.](image)
This structural evolution process is appreciably different from that detected for polyolefin like polyethylene, for example. In the latter case the random coils in the melt started to regularize after the temperature jump, and the trans-rich zigzag-like chains are formed with some conformational disorders. These chains gather together to form the pseudo-hexagonal lattice, which transforms gradually to the orthorhombic cell consisting of regular all-trans zigzag chain stems [5]. In this case the molecular chains are connected with weak van der Waals interactions. In the aliphatic nylon case, the methylene segments are constrained more or less due to the intermolecular hydrogen bonds even in the molten state. Therefore, some domains of comparatively high density are existent from the starting point of crystallization, making it easier to form the aggregation state of conformationally-regularized stems linked side by side with the strong intermolecular hydrogen bonds.

4. Conclusions

In the present report the structural evolution process of nylon 10/10 in the isothermal crystallization phenomenon has been revealed by measuring the time dependences of infrared spectra and synchrotron WAXD/SAXS data. The hydrogen bonds between the amide groups are existent even in the melted state although they are rather weak, which play an important role in the formation of domains with higher density. After the passage of some time, these domains gather together and transform to the stacked lamellar structure with regularly packed zigzag methylene segments combined with the strong intermolecular hydrogen bonds. This crystallization behavior is quite contrast to the case of polyethylene without any strong intermolecular hydrogen bonds. The difference in processability between these two kinds of polymer might reflect such a difference in crystallization process from the molten state.

Acknowledgements

This study was financially supported by a MEXT “Collaboration with Local Communities” project (2005 – 2009).

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