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Polymer Concepts in Microscopically-Viewed Phase Transition Behavior of Crystalline Polymers

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Summary: Structural evolution process in crystalline phase transition, isothermal crystallization from melt and solvent-induced crystallization has been investigated for crystalline polymers on the basis of the time and/or temperature dependence of small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS) and infrared/Raman spectra. As examples of isothermal crystallization study, polyethylene and polyoxymethylene were investigated. As for polyoxymethylene, the time-resolved infrared spectral measurement clarified the appearance of infrared bands characteristic of folded chain crystal (FCC) in the early stage of crystallization process, followed by the detection of infrared bands characteristic of extended chain crystal (ECC) in a later stage. From the time-resolved SAXS measurement, the stacked lamellar structure of ca. 14 nm long period was detected at first and it was followed by an appearance of the new lamellae in the amorphous region sandwiched between the original lamellae, resulting in the tightly stacked lamellar structure of 7 nm long period. The timing of detecting the SAXS 14 nm peak was almost the same with the observation of infrared FCC bands and the SAXS 7 nm peak with the infrared ECC band. This correspondency allowed us to speculate that some chains bridging several lamellae became fully extended when the new lamellae were formed in the amorphous region sandwiched between the original lamellae. As a result the ECC-like structural parts were formed, giving the ECC infrared bands. As other examples, the Brill transition of aliphatic nylons and the solvent-induced crystallization of syndiotactic polystyrene have been reviewed.

Keywords: Brill transition, isothermal crystallization, polyoxymethylene, solvent-induced crystallization, syndiotactic polystyrene

Introduction

One of the most characteristic structural features of a flexible polymer is a sensitive variation of its molecular conformation depending on the environmental condition. Typical example is seen in the phenomenon of polymorphism or the existence of various kinds of crystal

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modification. Besides, by changing such an external condition as temperature, stress, etc. the polymer chains experience phase transitions among these crystalline modifications. In the crystallization phenomenon also the polymer chains change their conformation remarkably from the random coil to the regular form. Such a drastic change of chain conformation results in remarkable change in the aggregation structure of the chains and also the change in higher order structure.

In order to understand the essential features of the phase transition and crystallization phenomenon, we need to obtain the information on the structural formation process as well as the structure itself. In other words we need to perform the time-resolved measurements of X-ray diffraction, infrared and Raman spectra, and so on. For the X-ray diffraction measurement, we can make a rapid collection of the one- and two-dimensional data by using a combination of quite powerful synchrotron radiation and highly-sensitive detector such as PSPC (position sensitive proportional counter) or CCD camera. Fourier-transform vibrational spectrometer allows us to make a rapid-scanning measurement of infrared/Raman spectra.

In the present paper we will describe the experimental results about the structural changes in the isothermal crystallization processes of POM and PE, in the solvent-induced crystallization of syndiotactic polystyrene (sPS) and in the Brill transition of nylons, which were obtained by utilizing the above-mentioned modern techniques.

Isothermal Crystallizations of POM and PE

POM is known to show characteristic infrared spectra, which are quite sensitive to the morphology of crystalline phase: folded chain crystal (FCC) and extended chain crystal (ECC).[1] These two kinds of POM sample show the infrared bands at the positions different by 100 cm^{-1}! By measuring the infrared spectra during the isothermal crystallization, therefore, we may trace the morphological change concretely. By combining this infrared spectral technique with the WAXS and SAXS methods, the structural change in the isothermal crystallization process of POM was investigated from the various points of view.

When the isothermal crystallization was performed at 130°C, the 1139 cm^{-1} infrared band of FCC morphology started to appear immediately after the temperature jump from the melt and increased in intensity with time. The 902 cm^{-1} band of ECC morphology was observed to appear around 150 sec later and increased in intensity. The time-resolved measurement of SAXS profile showed similar two-stages change. In the time region of detecting the FCC infrared bands, the SAXS peak (L_1) with the long period of ca. 14 nm started to appear. After that, the peak (L_2) of ca. 7 nm long period increased in intensity just when the infrared bands intrinsic of ECC morphology were detected, and the L_1 peak decreased in intensity in parallel. The generation of stacked lamellar structure of L_1 in the early stage of crystallization and the change to the lamellar structure with the long period almost a half of L_1 can be observed also in the crystallization of polyethylene.[2] These SAXS data could be interpreted reasonably in such a way that the amorphous region sandwiched between the original lamellae changes into a new crystalline lamella at the secondary crystallization stage (lamella insertion model). The SAS data were quantitatively analyzed on the basis of 1-dimensional lamellar stacking structure model with the second kind of paracrystalline disorder,[3] from which the structural information was obtained. By combining this information with the good correspondence between the X-ray and IR data (L_1 and FCC, and L_2 and ECC), we may derive the structural change shown in Figure 1 as a possibility. Immediately after an occurrence of crystallization, stacked lamellar structure with ca. 14 nm long period is generated. The molecular chains are folded and give the infrared bands of FCC. As the time passes furthermore, new lamellae are generated from the amorphous part sandwiched between the original lamellae. Some of the amorphous chain segments have a probability to pass through the neighboring two lamellae. When this amorphous region regularizes into a new lamella, the

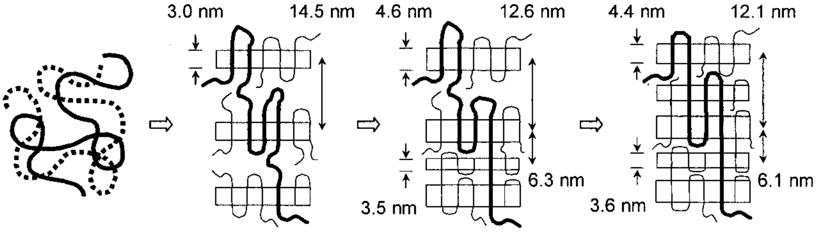

Fig. 1. A model of structural evolution process of POM in the isothermal crystallization at 130°C.

amorphous chain segment changes into straight stem and the total length of the extended segment becomes longer to form a taut tie chain.

Solvent-induced Crystallization of sPS

Amorphous sPS sample was exposed in an atmosphere of such organic solvent vapor as toluene.[4] The time dependence of infrared spectra was measured during this exposure. In parallel to the increment of toluene band intensity, the amorphous bands decreased in intensity and the crystalline bands characteristic of T_2G_2 helical chain conformation increased in intensity. Some of crystalline bands were found to appear earlier than some other crystalline bands. This phenomenon could be detected also in the Raman spectra. This detection time difference among the various bands is considered to come from a difference in sensitivity of an infrared (and Raman) band to the effective helical chain length or a difference in critical sequence length: a crystalline band can be detected for the first time when the length of a regular helical segment is beyond a critical value intrinsic of this band.[5] That is to say, the bands with relatively short critical sequence length were detected at first after injection of toluene, and the bands having longer critical sequence length were detected much later than the former bands, indicating a growth of helix. In parallel to this spectroscopic study, the time-resolved measurement of X-ray diffraction was made during exposure of the sample into a toluene gas. The timing to detect the X-ray diffraction intensity was almost the same with the timing to observe the Raman bands with long critical sequence length. Therefore, we may speculate that the random coils in the amorphous phase change at first into regular and short helical segments, which grow into longer helical sequences and gather together to form a crystalline lattice as being observed in the X-ray diffraction.

This solvent–induced crystallization of sPS was observed at room temperature, much lower than the original glass transition point (ca. 100°C). It may be easily speculated that the molecular motion in the amorphous phase is activated by a plasticizer effect of absorbed toluene molecules. In order to detect such a molecular motion experimentally, we measured the half-width of infrared amorphous band because the band width is inversely proportional to the relaxation time in general.[6] In fact, the half-width of the amorphous band became wider after injection of solvent, indicating a start of molecular motion. After that, for the first time, the crystalline bands with short critical sequence length began to appear. The half-width of the amorphous band became narrower again when the crystalline lattice was formed, indicating that the amorphous region was sandwiched between the crystalline lamellae and its motion was confined more or less due to some geometrical constraint.

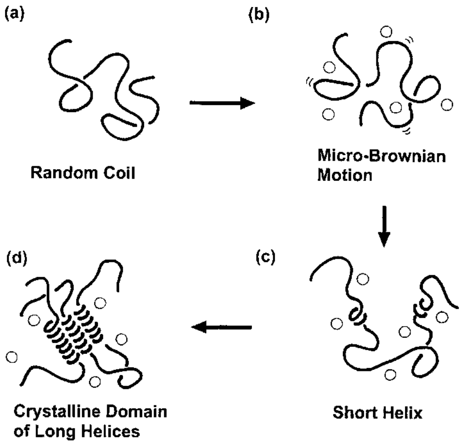

Fig. 2. An illustrated model of solvent-induced crystallization of sPS. Random coil starts to make a micro-Brownian motion by absorbing solvent (open circle). Then short helices are generated, grow longer and form a crystal lattice.

By combining all the experimental data mentioned above, a concrete image could be obtained for the solvent-induced crystallization phenomenon of sPS as shown in Figure 2. By absorbing toluene, the amorphous chains become mobile and change into regular short helical segments, which grow to longer helical sequences and form a crystalline lattice.

Brill Transition of Aliphatic Nylons

Many aliphatic nylons exhibit the so-called Brill transition phenomenon between the α form of triclinic structure and the pseudo-hexagonal form,[7, 8] but the details have not yet been clarified enough well. The conformational change in the methylene sequences is one of the most important problems to be solved about this transition. It was found to be possible to trace this conformational change by investigating the temperature change in a series of progression bands observed in the infrared spectra of aliphatic nylons.

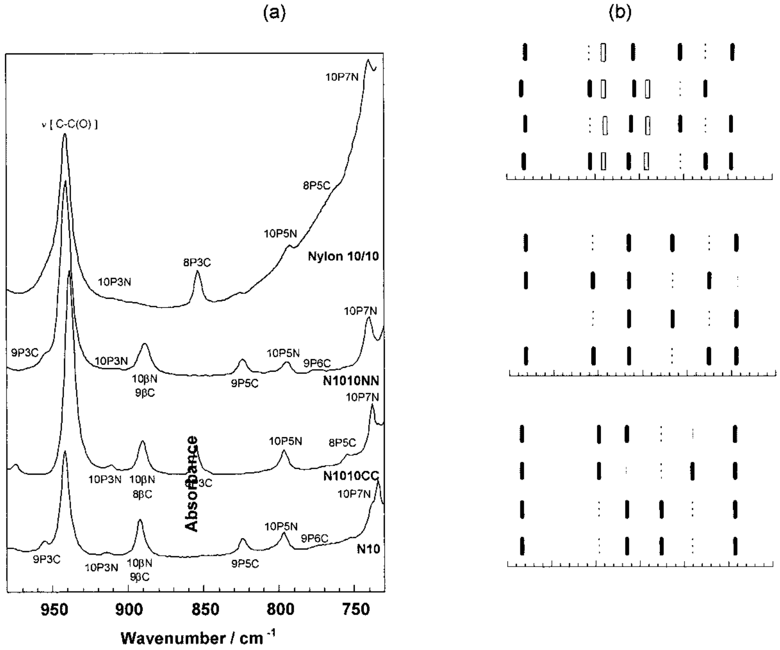

Fig. 3. (a) Observed infrared spectra of nylon 10/10 and its model compounds (refer to the text) in the CH_2 rocking region. The mark 8P5C, for example, indicates that this band is equivalent to the CH_2 rocking mode (P) with $k = 5$ of n-C_8H_{18}.(b) Comparison of the observed data with the predictions made by assuming the effective number of oscillators in different ways. The numbers [p, q] indicate the carbon numbers of equivalent n-alkane molecules including methyl end groups.

The progression bands are observed for a methylene segment of finite length as well known for n-alkanes and so on and can be interpreted on the basis of a simply-coupled oscillator model.[9] The vibrational frequency is a function of phase difference δ between the neighboring methylene units: $\delta = k\pi/(m + 1)$ where $k = 1, 2, \ldots, m$ and m is a total number of zigzag methylene units included in the stationary wave of the vibration. We have found that the progression bands observed for many nylon samples can be assigned reasonably by separating a methylene unit adjacent to the amide group from the other methylene sequence. For example, for nylon 10/10 -[-NH$(CH_2)_{10}$NHCO-$(CH_2)_8$-CO-]-, the observed progression bands can be assigned to the vibrational modes of methylene sequences of $(CH_2)_8$ (NH side) and $(CH_2)_6$ (CO side), not $(CH_2)_{10}$ and $(CH_2)_8$. Figure 3 shows this situation clearly. In Figure 3 (a) the infrared spectra observed for 4 types of sample (nylon 10/10 and its model compounds: N1010NN [$CH_3(CH_2)_8CONH(CH_2)_{10}NHCO(CH_2)_8CH_3$], N1010CC [$CH_3(CH_2)_9NHCO(CH_2)_8CONH(CH_2)_9CH_3$], and N10 [$CH_3(CH_2)_8CONH(CH_2)_9CH_3$]) are compared with each other. The positions predicted for several main bands are compared with the observed data as seen in Figure 3 (b). Prediction II is made by assuming all the methylene units as effective oscillators. Prediction I is based on the above-mentioned new concept. The latter gives a good agreement with the observed data. The methylene unit adjacent to the amide group is speculated to experience rather different thermal motion from that of the inner part of methylene sequence, resulting in the vibrational decoupling between them. Another possibility is a difference in electronic structure of methylene unit adjacent to the amide group from that of the inner part, giving different force constant and different vibrational frequency.

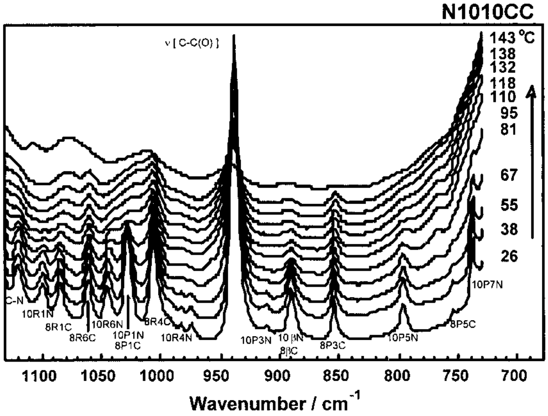

Fig. 4. Temperature dependence of infrared spectra of nylon 10/10 model compound (N1010CC, refer to the chemical formula given in the text).

The temperature dependence of these progression bands was measured. Above the Brill transition point, some of the progression bands disappeared and new progression bands appeared and increased in intensity as shown in Figure 4. At the same time the gauche bands were also detected. The generation of gauche bond shortens the long trans segment and the effective number of methylene units included in the trans-zigzag part becomes smaller. This change in methylene segmental length gives the change of phase difference and then the change of vibrational frequency. From the positions of the newly appeared bands, the average length of the thus shortened alkane segments could be estimated. In the case of Figure 4, for example, the trans-zigzag methylene segment is considered to change from $(CH_2)_{10}$ to $(CH_2)_7$ in average. In the Brill transition, the hydrogen bonds between the neighboring amide groups are not broken, as supported by the observation of hydrogen-bonded amide I band for example. Above the transition point the conformational disordering in the methylene segments is increased but under some constraints from the hydrogen bonds.

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