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Crystallization of poly(ethylene imine) amorphous sample in water vapor atmosphere

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Abstract

Infrared spectral measurement was carried out to find the crystallization of the amorphous poly(ethylene imine) (PEI) sample into the hydrates by absorbing water molecules. When PEI sample was melted and cooled to room temperature in dry state, it was found to crystallize into the anhydrate consisting of doubly stranded helices. But when the sample was melted and subjected to the humid atmosphere at the same temperature, the formation of hydrates was found to occur. The hydrates were considered to have higher melting points than the anhydrate, in other words, they were more stable than the anhydrate in higher temperature region.

Keywords: Poly(ethylene imine); Crystallization; Hydration

1. Introduction

Linear poly(ethylene imine) [PEI, $-(CH_2CH_2NH)_n-$] exhibits various types of crystalline hydrates in the humid atmosphere [1–3]. The anhydrate in the dry state consists of a parallel array of doubly stranded helices. The hydrates take the all-*trans* planar-zigzag chain conformation and exist in three types of crystalline modification: hemihydrate with molar ratio between ethylene imine (EI) monomeric unit and water EI/water = 1/0.5, sesquihydrate (EI/water = 1/1.5), and dihydrate (EI/water = 1/2). In this paper these crystal phases will be named anhydrate (0), hemihydrate (0.5), sesquihydrate (1.5), and dihydrate (2.0) to avoid any confusion.

Reversible and large conformational change between double helix and planar-zigzag form, which is caused by absorbing stoichiometric amount of water, is quite dramatic and the transformation mechanism must be clarified from the microscopic point of view. In the previous paper we carried out the time-resolved infrared spectral measurements of PEI in the hydration process [4]. When light water (H_2O) was used in the infrared spectral measurement, the broad bands of water overlapped the characteristic bands of hydrates, making it difficult to analyze the spectral changes in a quantitative manner. Then, heavy water (D_2O) was used instead of light water to reveal the crystalline bands of PEI by shifting the broad water bands to lower frequency region. As expected, many bands characteristic of anhydrate and hydrates could be extracted successfully, from which the infrared band intensities were evaluated as a function of time. Analysis of band profile was also made for the NH and ND stretching modes and the vibrational modes of water, allowing us to estimate the interaction between PEI and water molecules in various hydrates. In these experiments we noticed that the infrared bands characteristic of the amorphous region decreased in intensity in parallel to the intensity increment of the crystalline bands. This finding indicated that not only the crystalline region but also the amorphous region experiences the structural regularization to the hydrates. By extending this idea we may expect to observe a water-induced crystallization phenomenon for the totally amorphous PEI sample. The solvent-induced crystallization of amorphous sample was already reported for several such polymers as syndiotactic polystyrene (sPS) [5,6], poly(ethylene 2,6-naphthalate) [7], poly(ether ether ketone) [8], polycarbonate [9], nylon-61 [10], isotactic polypropylene [11] and aromatic polyimide [12] etc. In the sPS case, for example, by absorbing organic solvent an amorphous sPS sample crystallizes to the δ form which is a

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complex between the polymer of $(T_2G_2)_2$ helical conformation and solvent molecules. Our purpose is to confirm this solvent-induced crystallization phenomenon for the case of PEI–water system.

When we tried to prepare the pure amorphous sample of PEI, however, we could get only the partially crystalline sample by quenching the molten sample. Then we investigated the crystallization behavior of the molten PEI in the course of cooling from the melt. At first the cooling of the sample was made under dry state, which caused the crystallization of anhydrate. Secondly the crystallization was tried in the presence of some amount of water. Even at a temperature where no crystallization was induced under the dry state, the crystallization of hydrates was observed successfully to occur under the humid atmosphere. In this communication we will report the first observation of water-induced crystallization of the molten PEI. This finding is considered to be important for understanding a role of water molecules to stabilize the aggregation structure of PEI chains and a strong interaction between PEI and water.

2. Experimental

Linear PEI was prepared by alkaline hydrolysis of poly(*N*-acetyl ethylene imine) [13,14] supplied by Dow Chemicals Inc. A film sample of 10 μm thickness was sandwiched between a pair of KRS5 plates and sealed off to avoid the water leakage. One KRS5 plate had a small hole through which water was injected by a syringe. The KRS5 plates were set into a heater and the infrared spectra were measured during cooling from high temperature. The infrared spectra were measured by using a Bio-Rad FTS-60A FT-IR spectrometer equipped with an MCT (mercury–cadmium–telluride) detector at a resolution power of 2 cm^{-1}. For X-ray diffraction measurement the sample of ca. 2 mm thickness was prepared and set to a heater with a water reservoir. The time-resolved X-ray diffraction measurement was made by using a MAC Science DIP1000 system combined with a CCD detector (C4880-20, Hamamatsu Photonics Co. Ltd., Japan). The incident X-ray beam was a graphite-monochromatized Cu Kα line ($\lambda = 1.5418$ Å) from a MAC Science SRA18K rotating-anode-type X-ray generator.

3. Results and discussion

Fig. 1 shows the infrared spectral change measured for PEI sample in the cooling process from the melt in a dry atmosphere. As the temperature decreased, the bands of the melt decreased in intensity and the bands of the anhydrate (0) increased instead [4]. As long as no water was supplied to the sample, this process was reversible and the anhydrate (0) melted at 57 °C. Fig. 2 shows the infrared spectra in the cooling process from the melt to which some water was supplied. No band of the anhydrate (0) was observed but only the bands of the dihydrate (2) were detected. By applying the Lambert–Beer's law to the integrated intensity of infrared bands [4], the molar fraction of the crystalline phases was evaluated and was plotted against temperature as seen in Fig. 3. The molar fraction of the anhydrate (0) or the crystallinity was at most 40%, while the dihydrate (2) gained the crystallinity of about 90%. The crystallization in the dry state seems to be limited because of some entanglements in the amorphous region. But even such an amorphous region can be crystallized when some water is supplied [4]. Therefore, it may be reasonable to get higher crystallinity in the crystallization of the melt under humid atmosphere. Fig. 4 illustrates the structural change in the crystallization of anhydrate (0) and dihydrate (2) from the melt.

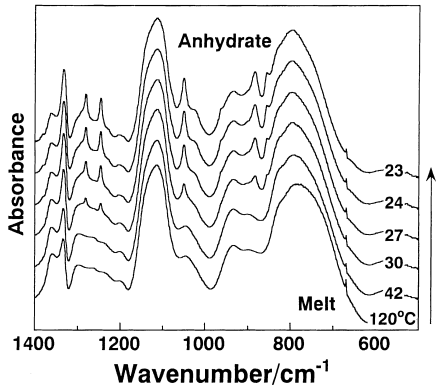

Fig. 1. Temperature dependence of infrared spectra of poly(ethylene imine) measured in the cooling process from the melt in the dry state.

The X-ray diffraction gave us more detailed change in the latter case. Fig. 5 shows the change of diffraction profile measured at 60 °C, higher than the melting point of the anhydrate (0). Only the halo peaks were observed at this temperature when the experiment was performed in the dry state. When some water was supplied to the system with the temperature fixed at 60 °C, the peaks of the hemihydrate (0.5) and the sesquihydrate (1.5) started to appear. Around 40–60 min after that, the transition from the hemihydrate

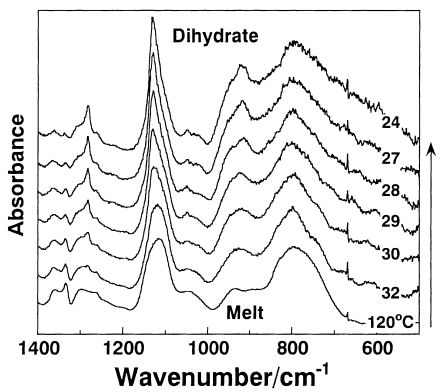

Fig. 2. Temperature dependence of infrared spectra of poly(ethylene imine) measured in the cooling process from the melt under the supply of water vapor.

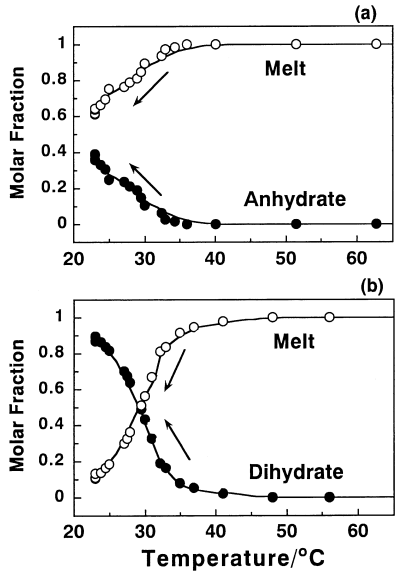

Fig. 3. Temperature dependence of molar fractions evaluated for (a) the anhydrate (0) in a dry state and (b) the dihydrate (2) in a humid atmosphere.

(0.5) to the sesquihydrate (1.5) was observed to occur. We might expect that the sesquihydrate (1.5) would transform to the dihydrate (2) after the passage of much longer time. In the infrared spectral measurement, since the thin film was used, the crystallization to the dihydrate (2) was observed immediately after the supply of water. But a utilization of thicker sample enabled us to observe the multiple transitions from the hemihydrate (0.5) to the dihydrate (2) in the X-ray diffraction experiment. It was because the penetration of water into the inner part of sample occurred relatively slowly than the case of infrared spectral measurement since a thicker sample was used in the X-ray experiment. In Fig. 5, it is noticed that the several peaks were detected as indicated by asterisks in the earliest stage of the crystallization. They could not be assigned to any peaks of the crystal

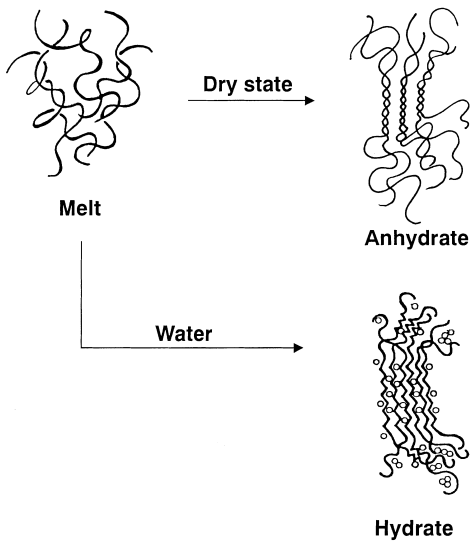

Fig. 4. A schematic illustration of the structure change in the crystallization process of poly(ethylene imine).

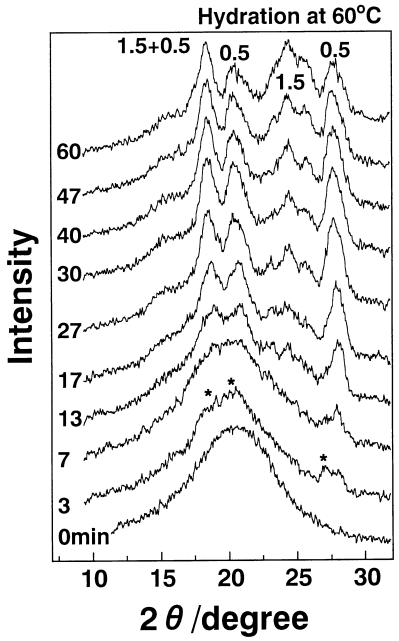

Fig. 5. Time dependence of X-ray diffraction profile of poly(ethylene imine) measured in the hydration process of the melt at 60 °C.

modifications of PEI reported so far [1–3] and might be due to another new crystalline form, although the concrete structure could not be clarified yet. As shown in Fig. 5 the hydrates could crystallize in the melting temperature region of the anhydrate (0), indicating that the hydrates are more thermally stable than the anhydrate (0) at 60 °C.

4. Conclusions

In the present paper we reported the first observation of water-induced crystallization of the molten PEI sample. This experiment allows us to speculate the thermal stability of hydrates in high temperature region compared with the anhydrate. The thermodynamic consideration may give us a useful information about the role of water molecules in stabilizing the hydrates. In the present paper we described only one example of water-induced crystallization of the molten PEI. By changing the temperature of the melt as well as the water content supplied to the sample, the various types of crystallization are expected to occur from the melt because the thermal stability might be different between the hydrates. The detailed experiment will lead us to draw a phase diagram of these crystalline modifications as a function of temperature and water content, as will be reported in a near future.

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