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Structural Study on Water-induced Phase Transitions of Poly(ethylene imine) as Viewed from the Simultaneous Measurements of Wide-Angle X-ray Diffractions and DSC Thermograms

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Summary: Thermal behavior of poly(ethylene imine) [PEI] has been studied using simultaneous WAXD/DSC measurement system. PEI exhibits water-induced and thermally-induced phase transitions among four kinds of crystalline hydrates: anhydrate (EI/water = 1/0), hemihydrate (1/0.5), sesquihydrate (1/1.5), and dihydrate (1/2). The chain conformation changes from a double helix in the anhydrate to a planar zigzag form in the three hydrates. The anhydrate melts at 60 °C while the hydrates melt differently in the temperature region of 70–110 °C. By means of the simultaneous WAXD/DSC measurements, complex DSC thermograms of PEI hydrates were characterized on the basis of X-ray diffractions obtained concurrently.

Keywords: hydrate; phase transition; poly(ethylene imine); thermodynamic

Introduction

Poly(ethylene imine) [PEI, $-(CH_2CH_2-NH)_n-$] exhibits water-induced phase transitions among four crystalline hydrates; anhydrate (EI/water = 1/0), hemihydrate (1/0.5), sesquihydrate (1/1.5), and dihydrate (1/2) as shown in Figure 1.[1] The chain conformation changes from a double helix, formed by the NH–N intermolecular hydrogen bonds, in the anhydrate to a planar zigzag form with the NH–O hydrogen bonds between water and polymer chains in the three types of hydrates.[1] Although such a large structural change is observed among the hydrates, the details of the transition behavior, especially the transition mechanism from double helix to a single chain, have not yet been revealed. To understand these transition mechanisms, we have studied the structural change in the phase transitions using a spectroscopic technique. Based on the infrared data, the above-mentioned transitions,[2] the water-induced crystallization in the amorphous region,[3] and the thermally-induced phase transitions among the hydrates[4] were revealed, from which the phase diagram of PEI/water system as functions of water content and temperature was obtained as shown in Figure 2.[4] On the basis of this phase diagram, we can predict the transition behavior controlled by the relative humidity and temperature. However, the thus-obtained phase diagram is still qualitative. We need to know the relationship between the molecular change, the change in molecular packing structure, and the thermal behavior for understanding the transition mechanism in more detailed manner. The X-ray diffraction study has not yet been made enough satisfactory, which should give us the detailed information about the crystal structural change during the transition process represented in Figure 2. Besides the thermal analysis is almost perfectly lacked in the study of PEI-water solid state transition phenomena. In this study, we have investigated the crystalline structure change in association with the

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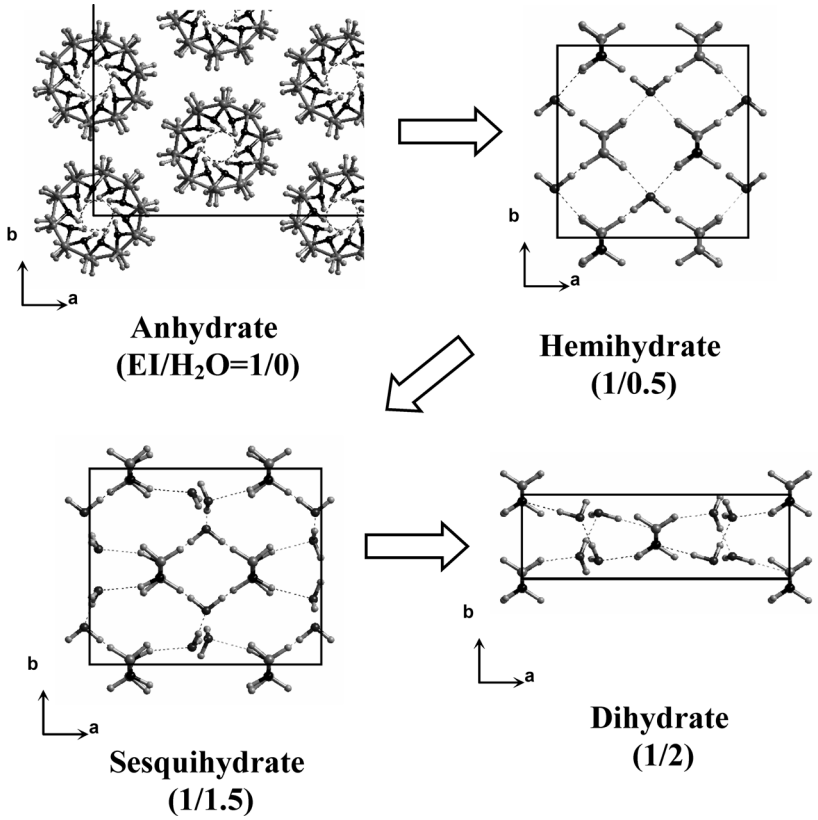

Figure 1.
Crystal structures of poly(ethylene imine).[1]

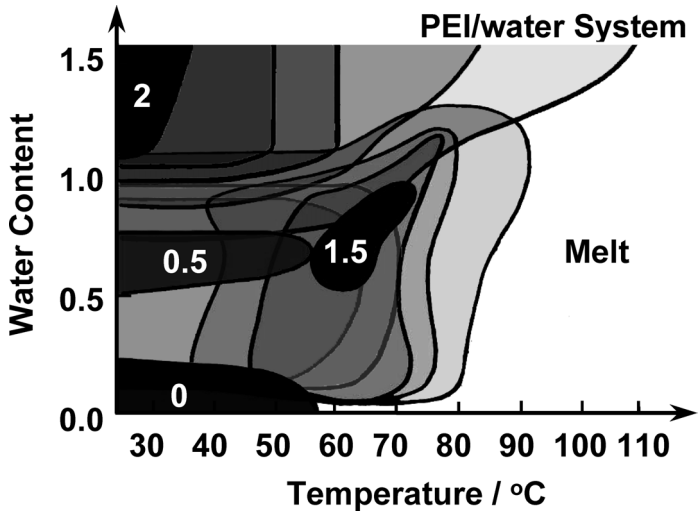

Figure 2.
Phase diagram of poly(ethylene imine).[4] Water content is only relative. For example, the anhydrate (0) containing small water content melts at around 60 °C. The dihydrate (2) with higher water content melts at around 110 °C.

thermodynamic data by means of simultaneous WAXD/DSC measurements.

Results & Discussion

Melting Behavior of Double Helix

The melting behavior of the anhydrate has been studied using simultaneous DSC/WAXD system and the infrared spectroscopy. Figure 3 (a) shows the DSC thermogram measured in the heating process of the dried sample. Figure 3 (b) shows the X-ray diffraction profiles measured simultaneously with the DSC thermogram. The melting peak at 66 °C is remarkably lower than those of the hydrates as seen from Figure 2. There detected a shoulder just below the melting peak in the DSC thermogram. As shown in Figure 4, the (620)/(040) reflection is found to become sharper in this temperature region. At the same time the lattice spacing becomes much larger. The similar change can be detected also in the infrared spectra. Figure 5 shows the temperature dependence of the various quantities estimated for the infrared NH streching band at 3200 cm^{-1}. As the temperature increases the peak position shifts toward the higher frequency side,

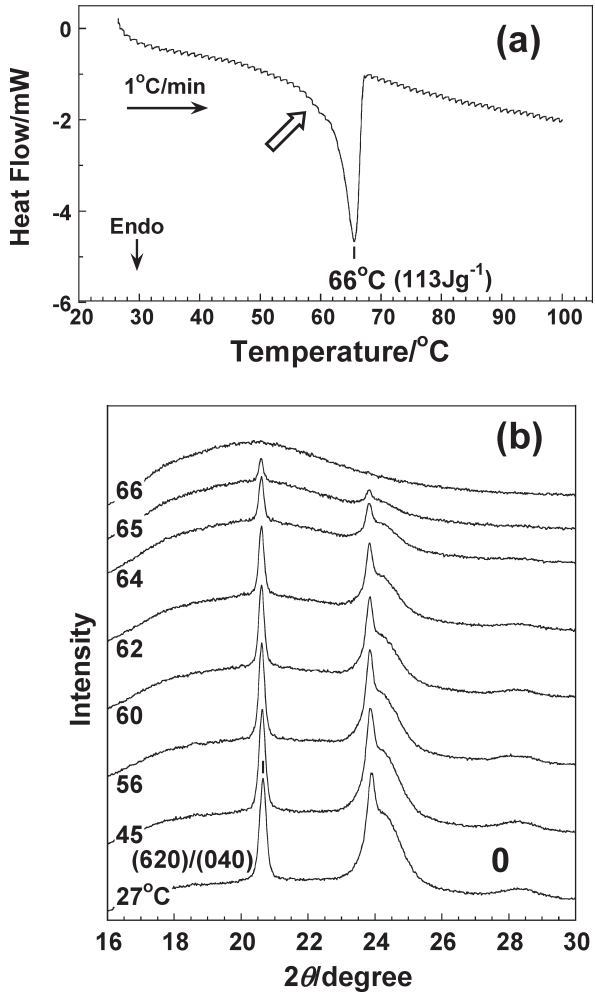

Figure 3.
(a) DSC thermogram of PEI dried sample. (b) WAXD profiles simultaneously obtained with the DSC thermogram.

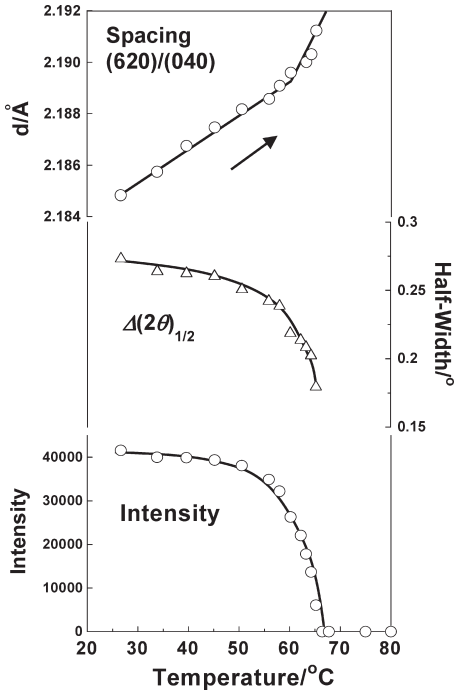

Figure 4.
Integrated intensity, half width, and d-spacing of the (620)/(040) reflection as a function of temperature.

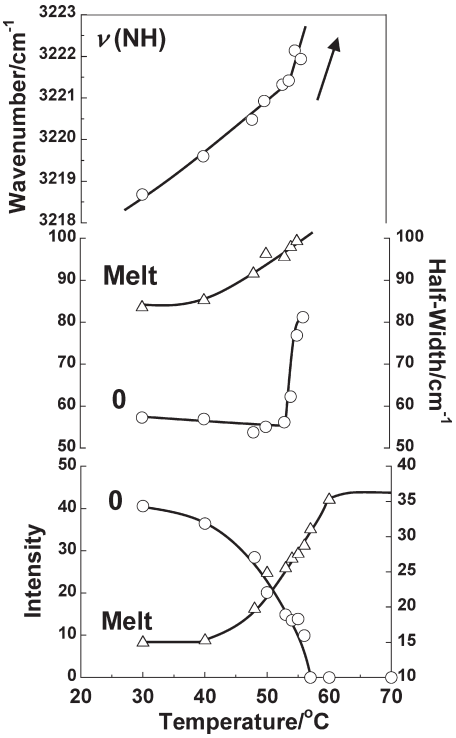

Figure 5.
Temperature-dependence of the peak position, half-width, and integrated intensity of NH stretching bands; the anhydrate (0) (○) and melt (△).

indicating the weakening of the intermolecular hydrogen bonds. A steeper change is detected above 55 °C: the higher frequency-shift and the increase of half width. Therefore the NH groups are suggested to be more mobile and the hydrogen bonds become much weaker. From these experimental data it is suggested the structure of anhydrate changes largely in the temperature region just below the melting point. There might be a possibility that the double helix loosens to separate into the single chains and melts at 66 °C.

Melting Behavior of Hydrated Samples

Figure 6 (a) shows the DSC thermogram measured in the heating process of the sample containing a small amount of water where the water included in the sample was almost perfectly sealed off not to escape from the sample pan. Figure 6 (b) shows the X-ray diffraction profiles measured for the same sample. In this experiment, the sample was wrapped with an alminum foil and sealed up using an adhesive not to evaporate the water inside similary to the case of Figure 6 (a). Figure 6 (c) shows the temperature dependence of integrated intensities of X-ray diffraction peaks obtained simultaneously with the DSC thermogram. The starting sample is considered to consist of the mixture of anhydrate (0) and hemihydrate (0.5) forms. By heating this sample, the anhydrate (0) starts to decrease in relative amount and transforms to the hemihydrate (0.5) in the temperature region of 50–60 °C. The anhydrate (0) peaks disappear totally above 60 °C. The hemihydrate (0.5) shows the plateau and then disappears above 80 °C. The three peaks observed in the DSC thermogram correspond well to the transition of $0 \rightarrow 0.5$, the melting of 0, and the melting of 0.5. In this case the water content is small, so the

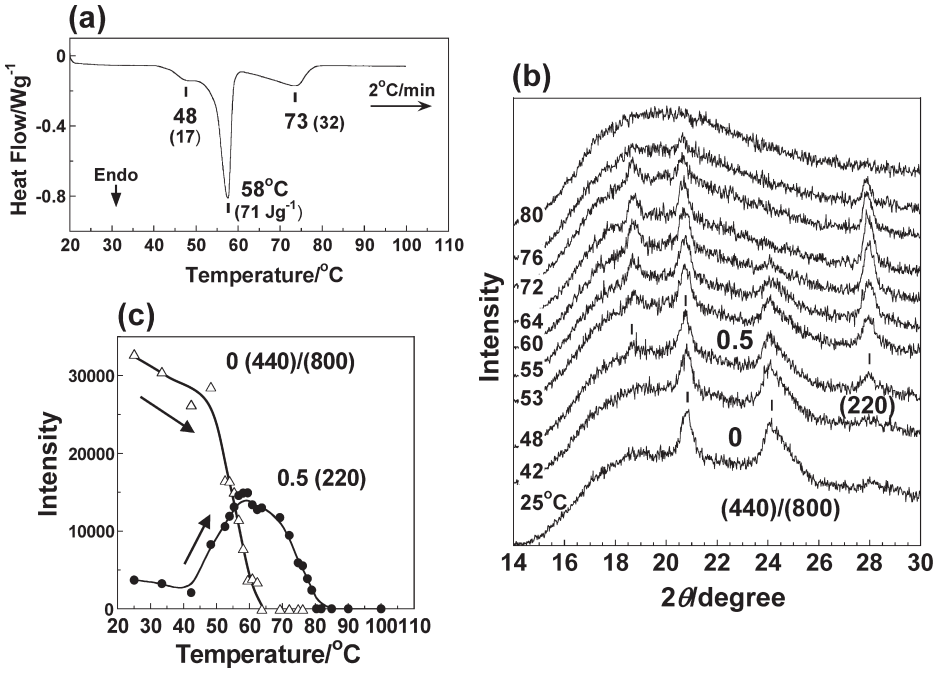

Figure 6.
(a) DSC thermogram of PEI hydrated sample. (b) WAXD profiles simultaneously obtained with the DSC thermogram. The decease in intensity below $2\theta = 18^\circ$ is caused by the beam stopper. (c) Temperature dependence of integrated intensities of the diffraction peaks of anhydrate (440)/(800), and hemihydrate (220).

transition to the hemihydrate (0.5) occurs only partially and many anhydrate (0) crystallites directly melt without transformation to the hemihydrate. This transition behavior is consistent with the prediction from the phase diagram given in Figure 2.

Figure 7 (a) shows the DSC thermogram measured in the heating process of hydrated sample. Figure 7 (b) shows the X-ray diffraction profiles measured simultaneously with the DSC thermogram where the sample was sealed off to avoid the water vapor leakage during heating. Figure 7 (c) shows the temperature dependence of integrated intensities of X-ray diffraction peaks. At 33 °C, the sample consists of the mixture of hemi- (0.5) and sesquihydrates (1.5). In the heating process, the hemihydrate (0.5) decreases and melts at 93 °C while the sesquihydrate (1.5) increases transiently in the temperature region of 60–80 °C and melts at 96 °C. The endothermic peaks at 93 and 96 °C in the DSC thermogram correspond to the melting phenomena of the hemihydrate (0.5) and the sesquihydrate (1.5), respectively. The exothermic peak at 75 °C corresponds to the phase transition from the hemihydrate (0.5) to the sesquihydrate (1.5).

The thermal behavior observed in the simultaneous WAXD/DSC measurements is not necessarily consistent with the phase diagram obtained by the infrared spectral experiment (Figure 2). In the infrared measurements, the sample of μm thickness was sandwiched between a pair of KRS5 plates and was sealed up with an adhesive. On the other hand, the sample for WAXD/DSC measurements was sealed using aluminum foils and an adhesive, but the leakage of water vapor seemed to occur relatively easily because of imperfect sealing. The change in water content during measurement results in the apparent inconsistency between the two types of experiment.

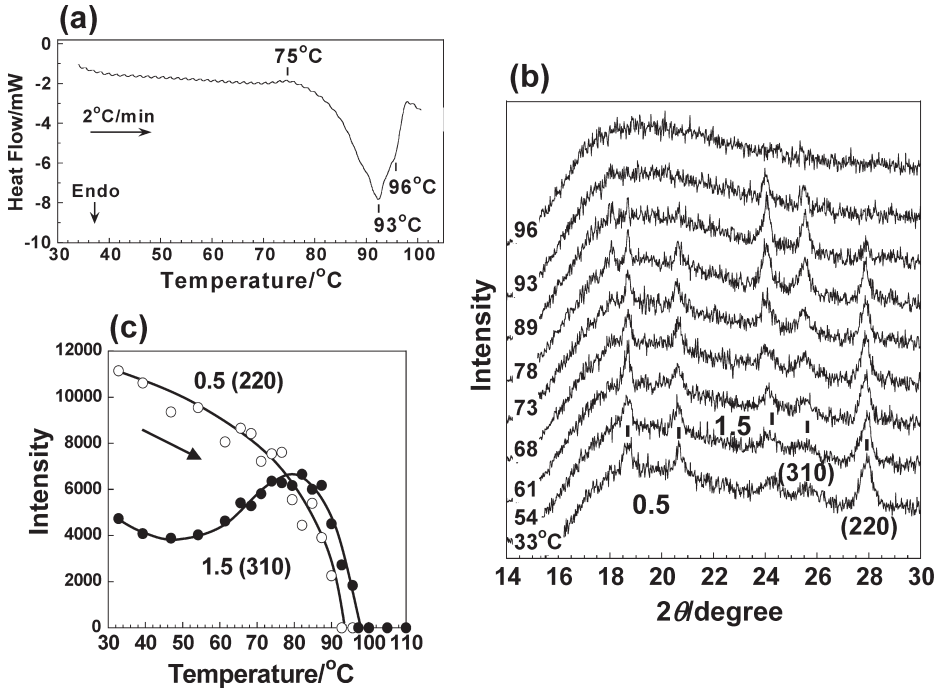

Figure 7.
(a) DSC thermogram of PEI hydrated sample with a larger amount of water. (b) WAXD profiles simultaneously obtained with the DSC thermogram. (c) Temperature dependence of integrated intensities of the diffraction peaks of hemi- (220) and sesquihydrates (310).

Conclusions

Thermal behavior of PEI has been studied using simultaneous WAXD/DSC system and infrared spectroscopy. Complicated DSC thermograms of PEI hydrates were characterized by the X-ray diffractions obtained concurrently. In the melting process of anhydrate (0), we have such a possibility that the double helices are loosened and change to the separated single chains with higher thermal mobility. In the heating process of the mixture of anhydrate (0) and hemihydrate (0.5), the transition from anhydrate (0) to hemihydrate (0.5) is found to occur in the temperature region of 50–60 °C. Three endothermic peaks at 48, 58, and 73 °C in the DSC thermogram were assigned to the transition of $0 \rightarrow 0.5$, the melting of 0, and the melting of 0.5, respectively. In a similar way, the DSC thermogram of heating process of the hemi- and sesquihydrate mixture was characterized reasonably.

The phase transition behavior is quite complicated. How about the relationship between the structural change in the crystalline lattice and the high-order structure or the lamellar stacking structure? We are now studying this problem by performing the simultaneous measurements of wide-angle and small angle X-ray scatterings in the hydration process.

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