Phase transition of hydrogen-bonded supermolecular assembly consisting of amphoteric molecules studied by DSC-XRD and DSC-FTIR

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Noncovalent bonding interactions such as hydrogen bonding, $\pi-\pi$ interaction, metal-legand interaction are used to assemble supermolecular architectures. One of the authors reported that amphoteric molecule which containing both donor and acceptor groups at both molecular ends formed fibrous supermolecular assemblages which were influenced by environmental factors such as ph of solution and temperature [1-3]. In biological systems, deoxyribonucleic acid forms supermolecular assemble optimising noncovalent bonding interactions by environmental factor. Azopyridine carboxylic acids have both a corboxyl group as a hydrogen donor and a pyridyl group as a hydrogen acceptor at each molecular ends form fibrous supermolecular assemble by head to tail hydrogen bonding. In this study, the structural transitions of supermolecular assembly consisting of azopyridine carboxylic acids in the bulk state were investigated by the simultaneous DSC-XRD and DSC-FTIR methods.

Sample used in this study was azopyridine carboxylic acids (C5PR) shown in scheme 1. Self-assemble fibres were obtained from 1mM aqueous solution of C5PR (pH=10.8) as precipitants by neutralization with carbon dioxide. Thermal properties of C5PR fibres were measured by DSC (SII model 6200 equipped with cooling apparatus), simultaneous DSC-

Scheme 1

XRD [4,5] and DSC-FTIR [6] used to determine the transition mechanism of C5PR supermolecular assembles. The simultaneous DSC was setting on XRD (Mac Science MXP06F) optics equipped with a CCD detector for DSC-XRD. FTIR used was JASCO FTIR 620 equipped with MCD detector for DSC-FTIR.
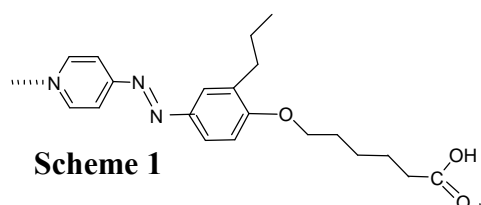
The scanning electron microphotograph of the self assemble C5PR fibres obtained as a precipitate from aqueous solution was shown in Fig. 1. The polarized FTIR microscopic measurement suggested that the azopyridine units, which connected by hydrogen bond between pyridyl and caboxyl groups, aligned parallel to the fibre axis. The length of fibre is in the order of cm and the aspect ratio is over 10^6. The fibrous texture was kept until 160 °C and changed to a bulky structure over 160 °C shown in Fig.2. The bulky structure was formed by coagulation of fibres and the fibre axis remained in the bulky crystal.
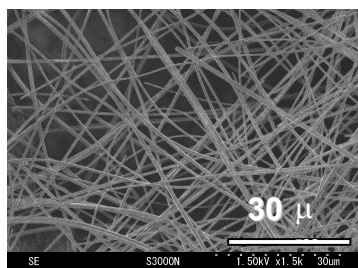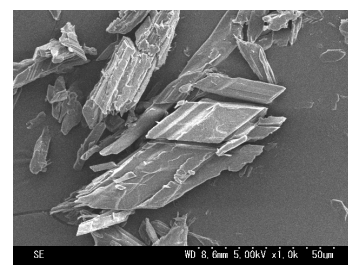
Fig. 1 Self assemble fibres of C5PR at room

Fig. 2 Self assemble architectures of C5PR at 160 °C

DSC heating curves of C5PR fibres are shown in Fig.3. The broad endothermic peak (ΔHtr_1 = 8.9 J g^{-1}) around 150 ^{o}C, which is non-thermo reversible transition, is observed only for the 1st measurement of C5PR fibre. The transition entropy (ΔStr_1) of this broad endothermic peak was 7.56 J K^{-1} mol^{-1}, this value corresponded to the deformation of hydrogen bonding. As shown in Figs. 1 and 2, the fibrous shape changed at this transition.

The endothermic peak (ΔHtr_2 = 144 J g^{-1}) at 170 ^{o}C is a thermo reversible transition. This transition is observed as an exothermic peak with about 20 ^{o}C of super-cooling on cooling at 10 kmin^{-1}. The values of this transition enthalpy (ΔStr_2) observed on 1st, 2nd and 3rd heating were almost the same (117.65 J K^{-1} mol^{-1}). This value is larger than the entropy change at fusion for an isotropic molecules and ionic crystals (20 – 50 J K^{-1} mol^{-1}). The entropy change at fusion is divided to three categories such as the entropy changes due to positional, orientational and conformational changes of molecules. Generally, the entropy of positional change is 7 – 14 J K^{-1} mol^{-1} and the entropy of orientaional change is in the order of 20 – 50 J K^{-1} mol^{-1}. In the case of polymer melting, the largest contribution on transition entropy is conformational change, as described by $\Delta S = Kln3^N$ (N indicated the degree of polymerisation).

Fig. 3. DSC heating curves of C5PR fibres at 1st, 2nd and 3rd runs from the lower DSC curve

DSC-XRD measurement was carried out for C5PR fibre at 1 Kmin^{-1}, and XRD profile change for the 1st heating was shown in Fig. 4. The crystal form of C5PR changed at the endothermic transition around 145 ^{o}C, and melted at 175 ^{o}C. The diffraction peak corresponding to the carboxylic acid dimer appeared at temperature above 150 ^{o}C, and it's intensity increased with increasing temperature. The XRD profile change around 145 ^{o}C and transition entropy suggested that this solid to solid transition was due to the change of orientation alignment induced by deformation of hydrogen bonding.

Fig. 4. XRD change of C5PR fiber obtained by DSC-XRD on heating at 1 Kmin^{-1}.

DSC-FTIR measurement was carried out to understand the melting mechanism of C5PR fibre. The DSC-FTIR results indicated that the carboxylic acid dimer increased after the transition at 145 ^{o}C, and the carboxylic monomer increased steeply at the melting. These results suggested that the supermolecular assembles of C5PR decomposed to carboxylic acid dimers and monomers by cleaving hydrogen bonds at the melting.

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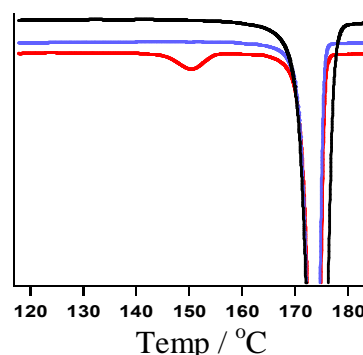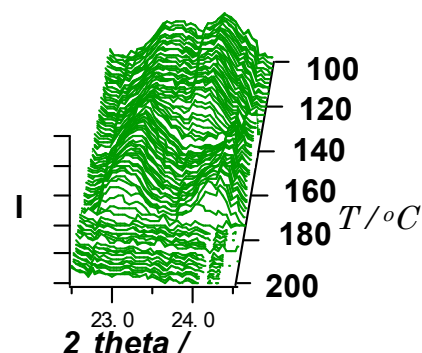6. H. Yoshida, *J. Thermal Analysis Calorimetry*, **55**, 679 (1999)