Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 569–573

DSC STUDIES ON THERMALLY INDUCED STRUCTURAL TRANSFORMATION OF HYDROGEN-BONDED AMPHOTERIC MOLECULAR ASSEMBLAGE

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Thermally induced structural transformation of fibrous hydrogen-bonded molecular assemblage formed from an amphoteric pyridinecarboxylic acid of 6-[2-propyl- 4-(4-pyridylazo)phenoxy]hexanoic acid (C5PR) was studied using differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TG). The organized fibrous morphology formed in an aqueous solution was stable at temperatures below 150°C. The ordered crystalline solid phase (K1) of the original fibrous material altered to a disordered crystalline solid phase (K2) at 150°C and subsequently to an isotropic phase (I) at 172°C. In the isotropic state, the C5PR molecule was slowly decomposed by decarboxylation. Once the molecular assemblage was subjected to the mesophase by heating, another ordered crystalline solid phase (K3) appeared reversibly at 17°C. The heat budget analyses by DSC indicated that a conformational entropy change such as the side-chain propyl group and the main-chain pentamethylene unit in the hydrogen-bonded molecular assemblage took place between the two ordered crystalline solid phases K1 and K3.

Keywords: *amphoteric compound, decarboxylation, DSC, DTA, fibrous material, hydrogen bond, liquid crystal, structural transition, supramolecular polymer, TG*

Introduction

Supramolecular architectures consisting of small organic molecules have attracted attention for the last decade. The reason comes from the following. First, morphologically fascinating nanostructures such as helical ribbons, fibers, tubes, capsule-included tubes are formed spontaneously from lipid-like molecules [1]. The self-assembly technique of organic molecules is one of bottom-up nanotechnologies, which is over top-down manufacturing nanotechnology. Secondly, it is possible to decompose the supramolecular architectures into original component molecules, because the supramolecular architectures are formed by non-covalent bonds having lower binding energies than covalent bonds. Reversible formation and cleavage of non-covalent bonds such as hydrogen bonds, metal-ligand coordination bonds, and van der Waals interactions will be useful tools of recycling and reusing the supramolecular architectures after use in materials science from a standpoint of green sustainable chemistry.

We have studied on self-assembly of amphoteric pyridinecarboxylic acids having a pyridyl group as a hydrogen bond acceptor and a carboxy group as a hydrogen bond donor at respective molecular terminals. When a pyridinecarboxylate in an alkaline aqueous solution is subjected to neutralization, fibrous molecular assemblage composed of the corresponding pyridinecarboxylic acid is formed [2]. The diameter of the fibrous material is highly dependent on chemical structure of the pyridinecarboxylic acids. We find out that some pyridinecarboxylic acid having an ethoxy group as a side-chain substituent forms a helical-ribbon structure with a helical pitch length of 1–2 μm. Using the morphology-tunable and recyclable fibrous molecular assemblages as templates to electroless plating, we have recently demonstrated that a new method for fabricating hollow nickel-phosphorus (Ni/P) microfibers [3]. To reveal what factor determines the diameter and the macroscopic organized morphology, we were led to a conclusion that hierarchical non-covalent interactions composing the fibrous molecular assemblages should be comprehended. Moreover, the thermal stability should be confirmed to use the hydrogen-bonded molecular fibers as reliable template materials.

In this study, we investigated the thermally induced structural transformation of the hydrogen-bonded molecular assemblage formed from 6-[2-propyl-4-(4-pyridylazo)-phenoxy] hexanoic acid (C5PR) as shown in Fig. 1. The heat budget determined by DSC will make clear the thermo-stable hier-

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1388–6150/$20.00

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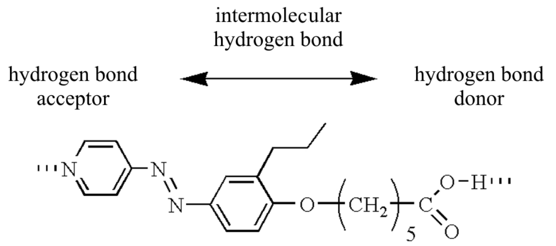

Fig. 1 Chemical structure of C5PR

archy of non-covalent interactions in the hydrogen-bonded molecular assemblage. TG/DTA analyses will reveal the thermal stability of the fibrous material.

Experimental

Preparation of hydrogen-bonded supramolecular assemblages

6-[2-Propyl-4-(4-pyridylazo)phenoxy]hexanoic acid (C5PR) was prepared according to our previous report [2]. An alkaline solution containing 1.0 mmol dm^{-3} C5PR and 2.0 mmol dm^{-3} NaOH was kept standing for under an air atmosphere. After 3 days, the orange transparent solution of pH 12.0 turned to a yellow suspension of pH 8.5 containing fibrous molecular assemblage. The fibrous material was filtered, rinsed with distilled water, and freeze-dried. The freeze-dried fibrous material was subjected to DSC and TG/DTA measurements.

Instrumentation

The heat budget analysis of C5PR fibrous molecular assemblage was carried out by DSC (Seiko DSC-6200) equipped with a cooling apparatus. 5.00 mg of the sample was heated and cooled at a rate of 10°C min^{-1} from –100 to 200°C under a nitrogen atmosphere. The thermal decomposition was carried out by TG and DTA (Seiko TG/DTA-6300). 15.0 mg of the sample was heated at a rate of 10°C min^{-1} from 50 to 500°C under a nitrogen atmosphere. To investigate the effect of the C5PR thermal decomposition after isotropic phase transition on the DSC analyses, the heated sample was held at 200°C for 30 min. Morphological changes of the C5PR fibrous material at elevated temperatures were observed by an optical microscope (Olympus BX-60) equipped with a hot stage (Mettler FP-90) and a CCD camera (Olympus DP-70).

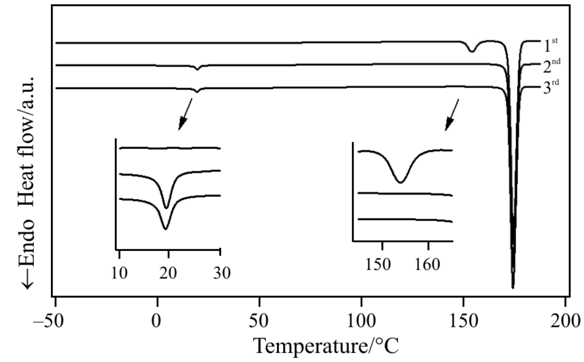

Fig. 2 DSC curves of C5PR molecular assemblage on heating at 10°C min^{-1} without a retention time at 200°C

Results and discussion

Phase transition of hydrogen-bonded supramolecular assemblages

Figures 2 and 3 show the DSC heating and cooling curves of the C5PR fibrous molecular assemblage at a rate of 10°C min^{-1}. On 1st heating, two endothermic transitions were observed around 150 and at 172°C. To assume what structural transition occurred at elevated temperatures, we observed the thermal change in macroscopic morphology of the C5PR fibrous material using an optical microscope with a hot stage. The fibrous morphology was maintained below 150°C as shown in Fig. 4a. The long axis of the C5PR fibers began to shrink at 160°C for 2 h as shown in Fig. 4b, and eventually the fibrous material become isotropic liquid at 172°C. These optical microscopic observations indicated that the molecular assemblage transformed to another crystalline phase in the range of 150–172°C. On 1st cooling from 200°C, two exothermic transitions were observed at 158 and 17°C.

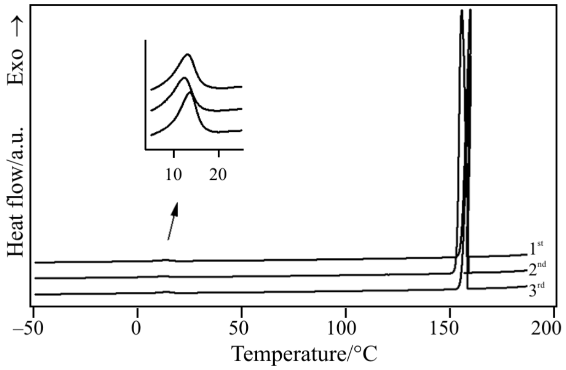

Fig. 3 DSC curves of the C5PR molecular assemblage on cooling at 10°C min^{-1} without a retention time at 200°C

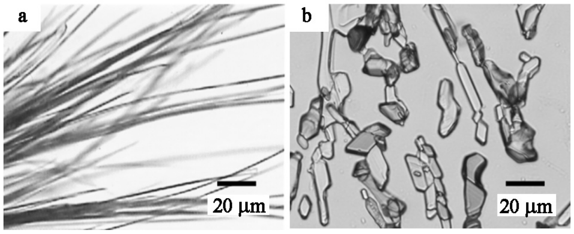

Fig. 4 Optical microscope images of a – fibrous molecular assemblage below 150°C and b – at 160°C for 2 h

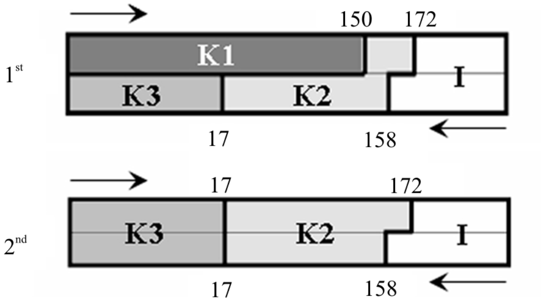

Fig. 5 Phase transition of C5PR molecular assemblage

When the freeze-dried fibrous material was heated to 140°C and cooled to –100°C, the exothermic transition at 17°C could not be observed. On the other hand, when the freeze-dried fibrous material was heated to 160°C, we could observe the exothermic transition at 17°C. These DSC analyses of the C5PR fibrous material clearly indicated that the small endothermic transition around 150°C on 1st heating had a relation to the exothermic transition at 17°C on 1st cooling. Since 2nd heating and cooling processes, the endothermic transitions at 17 and 172°C, and the exothermic transitions at 158 and 17°C were observed reversibly.

To discuss thermal properties, we determined transition enthalpy (ΔH) and transition entropy (ΔS) at each transition. Here, the transitions at 150 and 172°C on 1st heating are abbreviated as transition I (trI) and transition II (trII), respectively. The transitions at 17 and 172°C on 2nd heating are abbreviated as transition III (trIII) and transition IV (trIV), respectively. The transition I at 150°C was attributable to a non-thermo reversible transition. The transition enthalpy and entropy at transition I were ΔH_{trI}=8.90 J g^{-1} and ΔS_{trI}=7.56 J K^{-1} mol^{-1}. The transition II at 172°C to isotropic liquid was attributable to a thermo reversible transition with ΔH_{trII}=144 J g^{-1} and ΔS_{trII}=118 J K^{-1} mol^{-1}. The value of ΔS_{trII} was almost consistent with ΔS_{trIV}=118 J K^{-1} mol^{-1} observed for 2nd and 3rd heating processes. The transition III at 17°C after experiencing the transition I was a thermo reversible transition with $\Delta H_{\mathrm{trIII}}$=3.62 J g^{-1} and $\Delta S_{\mathrm{trIII}}$=4.44 J K^{-1} mol^{-1}.

The phase transition temperature of the C5PR fibrous molecular assemblage formed in an aqueous solution is summarized in Fig. 5. The fibrous material was assignable to a crystalline state (K1) as similarly observed for crystalline polymer solids, because we previously observed some crystalline diffraction peaks and an amorphous peak in the XRD pattern of the fibrous material [2]. The fibrous material showed another crystalline state (K2) with low molecular ordering to the fibrous material in the range of 150–172°C and an isotropic phase (I) over 172°C on 1st heating. On 1st cooling, the isotropic state (I) was changed to the low-ordering crystalline state (K2) again. This is because the transition entropy at 172°C on heating (ΔS_{trII}=118 J K^{-1} mol^{-1}) was consistent with that at 158°C on cooling (ΔS=118 J K^{-1} mol^{-1}). It is worthy of note that the transition entropy at 17°C ($\Delta S_{\mathrm{trIII}}$=4.44 J K^{-1} mol^{-1}) is significantly smaller than that at 150°C on 1st heating (ΔS_{trI}=7.56 J K^{-1} mol^{-1}). These thermal analyses obviously suggested that the original fibrous molecular assemblage before heating had higher molecular ordering than the molecular assemblage below 17°C on 1st cooling. Taking account into the fact, the molecular assemblage below 17°C should be assigned to another crystalline solid phase K3 different from K1.

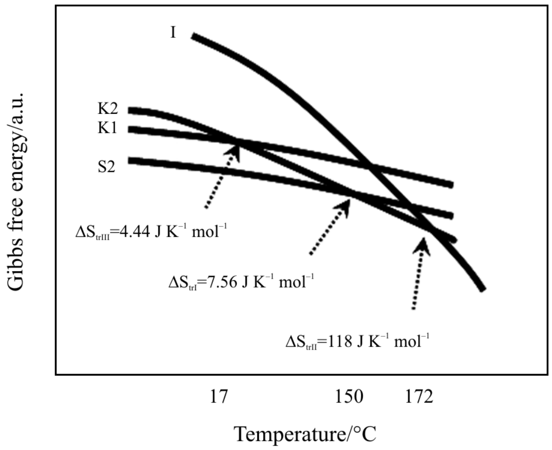

Fig. 6 Model of Gibbs free energy changes of C5PR molecular assemblage

A second noticeable point is that the value of the transition entropy (ΔS_{trII}=118 J K^{-1} mol^{-1}) to an isotropic phase was significantly larger than general transition entropies at fusion observed for crystals of anisotropic rigid molecules (7–14 J K^{-1} mol^{-1}) and ionic crystals (14–28 J K^{-1} mol^{-1}). An entropy change can be divided to three entropy changes attributable to positional, orientational, and conformational changes of component molecules. A positional entropy change is in the range of 7–14 J K^{-1} mol^{-1}. An orientational entropy change is in the range of 20–50 J K^{-1} mol^{-1}. When a polymer solid is melted, a large amount of conformational entropy change of component macromolecules is dominant in the transition entropy at fusion. Taking account of the facts, the large transition entropy at transition II is probably due to a conformational entropy change of hydrogen-bonded supramolecular polymers in the low-ordering crystalline state (K2).

As a summary of the DSC measurement, we would like to propose a possible change in the Gibbs free energy of the C5PR hydrogen-bonded molecular assemblage as a function of temperature as shown in Fig. 6. The ordered crystalline solid phase (K1) of the original fibrous material shifted down to the low-or-

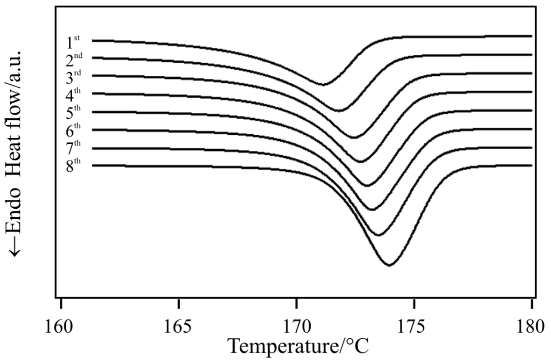

Fig. 7 DSC curves of C5PR molecular assemblage on heating at 10°C min^{-1} with a retention time at 200°C for 30 min

dering crystalline state (K2) and to the isotropic phase (I). Once the molecular assemblage was subjected to the mesophase, the mesophase was back to another crystalline solid phase (K3). The successive head-to-tail intermolecular hydrogen bonds between the pyridyl and carboxy groups of C5PR are cleaved in the isotropic phase according to our previous study [2]. Taking account of the small entropy change of transition I at 150°C, we assumed that the transition I is not responsible for the cleavage of the hydrogen bonds. A conformational entropy change such as side-chain propyl group and the main-chain pentamethylene unit in the hydrogen-bonded supramolecular polymer of C5PR should be considered. To comprehend the transitions I at 150°C and IV at 17°C in detail, DSC-FTIR [4] and DSC-XRD [5, 6] simultaneous measurement methods will be powerful tools.

Thermal decomposition of C5PR molecule

The transition enthalpy at transition II to an isotropic liquid state was observed reversibly on 2nd and 3rd heating at a rate of 10°C min^{-1} without time interval at 200°C. In contrast, as seen in Fig. 7, the clearing point at 172°C continued to decrease, concomitantly with a decrease of the transition enthalpy, the annealing temperature was held at 200°C for 30 min. This result obviously indicated that some thermal decomposition of the C5PR molecule took place during the isotropic liquid phase.

Kocaokutgen *et al.* have reported that aromatic azo compounds of 4-hydroxy- 4'-nitroazobenzene derivatives were decomposed thermally to 280°C [7]. Kim *et al.* have reported that carbon dioxide was formed from aliphatic carboxy groups at a high temperature above 200°C [8]. The C5PR molecule used in this study has both an aromatic azo moiety and an aliphatic carboxy group. To investigate what molecular segment of the C5PR molecule was broken in the isotropic state, the thermal decomposition was followed by TG/DTA analysis and FTIR measurement.

Figure 8 indicates the TG and DTA curves of the C5PR fibrous material on heating rate of 10 K min^{-1} from 50 to 500°C. Small mass loss started over the clearing point at 172°C. Subsequently, two steps of large mass loss took place at about 270 and 400°C. The second mass loss was approximately 30 mass% by 320°C, and the third mass loss involved about 50 mass% by 450°C. Owing to partial sublimation of the C5PR molecule together with the thermal decomposition, it was difficult to determine a decomposed molecular segment by the TG analysis.

Parts Fig. 9a and Fig. 9b of Fig. 9 show the FTIR spectra of fibrous material before and after annealing at 180°C for 15 h. The original C5PR fibrous material exhibited three characteristic absorption peaks consisting of an C=O stretching vibration band ($\nu_{C=O}$), around 1700 cm^{-1}, an O–H stretching vibration band ($\nu_{O\text{-}H}$) at 2500 cm^{-1}, and Fermi sympathetic vibration band at 1900 cm^{-1} [9]. The spectroscopic feature means that intermolecular hydrogen bonds were formed between the pyridyl and carboxy groups. In contrast, as seen in Fig. 9b, the three characteristic absorption peaks disappeared in the annealed C5PR molecular assemblage. Moreover, a new characteristic peak at 1580 cm^{-1} appeared. The peak was attributable to a ring stretching vibration of hydrogen-bonding free pyridyl group. These results clearly suggested that relatively slow thermal decomposition of the carboxy group was brought about over the melting

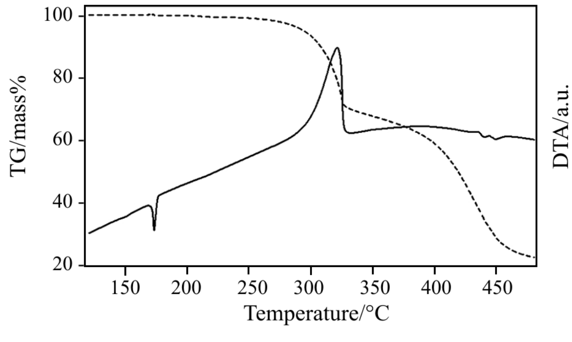

Fig. 8 DTA (solid line) and TG (dotted line) curves of C5PR molecular assemblages on heating at 10°C min^{-1}

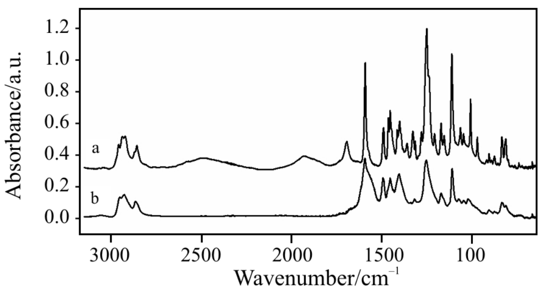

Fig. 9 FTIR spectra of a – original fibrous molecular assemblage and b – molecular assemblage annealed at 180°C for 15 h

point. The decomposed species induced the depression of the melting point on the 2nd and 3rd heating process observed for the DSC measurement.

Conclusions

We demonstrated the thermally induced structural transformation of hydrogen-bonded molecular assemblages formed from C5PR molecules by means of DSC and TG measurements. The phase transition to low-ordering crystalline state was observed around 150°C, and thermo reversible transition to isotropic phase was observed at 172°C. The crystalline structure (K3) having weaker molecular interaction than original fibrous molecular assemblages (K1) was formed from low-ordering crystalline state (K2) by cooling. Over 172°C, the C5PR molecule was slowly decomposed by decarboxylation. To comprehend the conformational changes by heat treatment in detail, it is necessary to measure X-ray structural analysis and FTIR measurement with the simultaneous DSC measurement.

References

1 J.-H. Fuhrhop and T. Wang, Chem. Rev., 104 (2004) 2901.
2 K. Aoki, M. Nakagawa and K. Ichimura, J. Am. Chem. Soc., 122 (2000) 10997.
3 D. Ishii, K. Aoki, M. Nakagawa and T. Seki, Trans. Mat. Res. Soc. Jpn., 27 (2002) 517.
4 H. Yoshida, J. Therm. Anal. Cal., 55 (1999) 679.
5 H. Yoshida, R. Kinoshita and Y. Teramoto, Thermochim. Acta, 264 (1995) 173.
6 G. Z. Zhang, T. Watanabe, H. Yoshida and T. Kawai, Polymer J., 35 (2003) 188.
7 H. Kocaokutgen and I. E. Gumrukcuoglu, J. Therm. Anal. Cal., 71 (2003) 675.
8 S. J. Kim, K. J. Lee, S. M. Lee, I. Y. Kim, Y. M. Lee and S. I. Kim, J. Appl. Polym. Sci., 88 (2003) 2570.
9 T. Kato, J. M. J. Frechet, P. G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin and F. Fujishima, Chem. Mater., 5 (1993) 1094.

DOI: 10.1007/s10973-005-7083-z