Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 3, 681–685

THERMALLY INDUCED STRUCTURAL TRANSFORMATION IN A HYDROGEN-BONDED SUPRAMOLECULAR SINGLE-CRYSTAL
DSC-FTIR studies

D. Ishii[1]*, *T. Yamada*[2], *M. Nakagawa*[1], *T. Iyoda*[1,3] *and H. Yoshida*[2,3]

[1]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta Midori-ku, Yokohama 226-8503, Japan
[2]Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan
[3]CREST-JST, 4-1-8 Honmachi, Kawaguchi, Saitama 332-0012, Japan

The thermally induced structural transformation of a hydrogen-bonded crystal formed from an amphoteric molecule of 6-[2-methoxy-4-(pyridylazo)phenoxy]hexanoic acid MeO was studied using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction measurement (XRD). Crystal form of the hydrogen-bonded crystal was measured by single crystal four circle diffractometer (Mo-K_α radiation). As a result, the crystal of MeO was stabilized by many C–H···O hydrogen bonds, and the C–H···O hydrogen bonds were broken by thermal energy reversibly. After transformation the supramolecular architecture was composed of supramolecular polymer including free-rotation pentamethylene main chains.

Keywords: *amphoteric compound, C–H···O, crystal structure, DSC-FTIR, hydrogen bond, rotator phase, structural transition, supramolecular polymer*

Introduction

Supramolecular architectures formed from a small molecule by self-assembly are stabilized thermodynamically by non-covalent bonds [1, 2]. A binding energy of a non-covalent bond is about one tenth weaker than that of a covalent bond, so that a conformational transformation of supramolecular architectures is easily induced by a small thermal energy.

We have reported that a hydrogen-bonded self-organized fiber having a diameter of 500 nm is spontaneously formed from 6-[2-propyl-4-(4-pyridylazo)phenoxy]hexanoic acid Pr having a propyl group on a phenyl ring [3]. The self-organized fiber formed in an aqueous solution is composed of one-dimensional head-to-tail O–H···N hydrogen bonds between carboxy group as a hydrogen bond donor and the pyridyl group as a hydrogen bond acceptor [4]. Self-organized fibers with a twisted structure or a different outer diameter are obtained from similar amphoteric molecules having a different substituent group instead of the propyl group [5]. The fibrous morphology is transformed by heat treatment [6], and the orientation of azo units is dramatically changed after the structural transformation [7]. The supramolecular single crystal of the same molecule was prepared by sublimation [8] and the thermo-stable hierarchy of its crystal was revealed in our proceeding [9]. As results of our recent studies we found out that these behaviors were brought out by an influence of main- and side-chain methylene conformations [8].

Here we thought that to leave the influence of methylene interdigitation of side-chain propyl group off, we used 6-[2-methoxy-4-(pyridylazo)phenoxy]hexanoic acid MeO having side-chain methoxy group as shown in Fig. 1. In this paper we investigated a thermally induced structural transformation of a hydrogen-bonded single crystal of MeO prepared by sublimation. Compared with Pr having side-chain propyl group, amphoteric molecule MeO has simple side-chain group of methoxy group which does not have any methylene groups. Therethrough a behavior of only methylene main chain will be carried out by a DSC-FTIR and temperature-controlled XRD measurements.

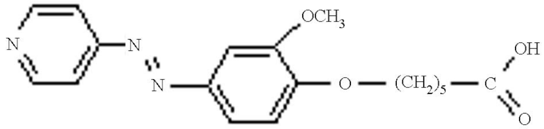

Fig. 1 Chemical structure of MeO

Experimental

Preparation of hydrogen-bonded supramolecular crystal of MeO

6-[2-methoxy-4-(pyridylazo)phenoxy]hexanoic acid MeO prepared according to our previous report [4] of 1.0 g was placed in a glass sample vessel (30 mL), whose flat bottom was heated at 200°C for 20 h under a reduced pressure of 160 mmHg. Orange single crystals were formed by sublimation around a wall of the

---

* Author for correspondence: dishii@riken.jp

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

glass vessel and collected. The structural analysis was performed by a single crystal four-circle diffractometer with Mo-K$_{\alpha}$ radiation of 0.71070 Å (Rigaku Saturn 70 CCD system).

Instrumentation

Thermodynamic properties of MeO 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 220°C under a nitrogen atmosphere. The thermally induced conformational transformation of the crystal was investigated by a simultaneous DSC-FTIR measurement which was performed using a simultaneous DSC instrument equipped with a Jasco FTIR 620 [10]. The crystal was grind down with dried KBr powder and pressed to make a crystalline pellet. A heating rate of 2°C min^{-1}, an IR sampling rate of 1 scan min^{-1}, a scan resolution of 2 cm^{-1} and a time interval of 50 s were used. The thermally induced changes of lattice intervals in the supramolecular crystal were measured by a MAC Science M21X-SRA XRD with Cu-K$_{\alpha}$ radiation of 1.5405 Å equipped with a temperature-control system.

Results and discussion

Crystal structure of 6-[2-methoxy-4-(pyridylazo)phenoxy]hexanoic acid MeO

An orange leaflet single crystal of MeO could be prepared by sublimation, and its crystal structure could be determined by X-ray structural analysis. The ORTEP image (30% thermal ellipsoids) and the crystal packing viewed along the *a* axis of MeO (Mw=343.38) were shown in Figs 2 and 3, respectively. The crystal system was triclinic with space group of P-1(#2). The lattice parameters were a=4.5417(9) Å, b=13.497(2) Å, c=14.106(3) Å, α=76.189(7)°, β=81.160(6)°, γ=83.884(8)°, V=825.5(3) Å^3, Z=2, D_c=1.378 g cm^{-3}, with structure reliability factors R_1, I>3σ(I)=0.038 and wR_2, I>3σ(I)=0.060. X-ray analysis of the single crystal in Fig. 3 indicated the molecular long axis of MeO aligned along the 011 plane, and each molecule along the 011 plane were head-to-tail orientation between the pyridyl and carboxy groups. Steiner reported the geometric parameters in general hydrogen bonds such as O–H···O, O–H···N, and the other hydrogen bonds. Most of O–H···N hydrogen bonds possess O···N distance (D) of 2.6–3.1 Å, H···N distance (d) of 1.5–2.1 Å, and O–H···N angle (α) of 170–180° [11]. The single crystal of MeO possessed the liner O(3)–H···N(1) bond (D=2.61 Å, d=1.53 Å, and α=171°), so that the general intermolecular hydrogen bond between the pyridyl group and the carboxy group composed a supramolecular main chain along the 011 plane. To focus on the 01–1 plane, the head-to-tail supramolecular main-chains were collocated with antiparallel orientation. Spacing at –160°C between the supramolecular main-chains which was attributable to a 011 surface with the highest electronic density was 5.36 Å. In the amphoteric molecule Pr having a propyl group, an interval among the double strand was 6.07 Å. Moreover a crystal density of MeO with 1.378 g cm^{-3} was higher than that of Pr with 1.235 g cm^{-3}. These results obviously suggested that the MeO single crystal possessed higher dense crystal packing than the Pr single crystal.

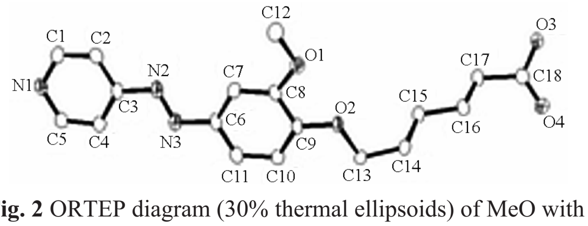

Fig. 2 ORTEP diagram (30% thermal ellipsoids) of MeO with atomic labels for the molecule used throughout the text

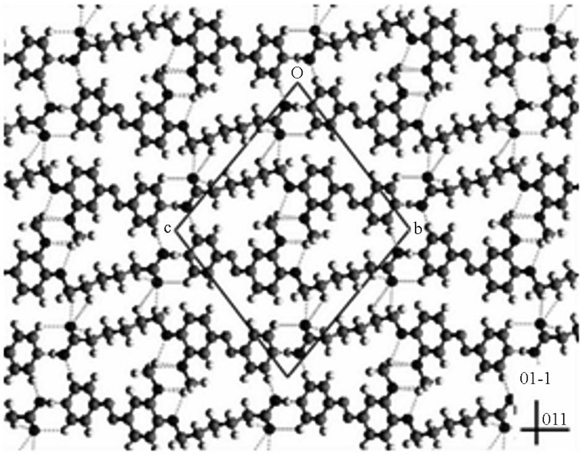

Fig. 3 Crystal packing of MeO viewed along the *a* axis. Dashed lines indicate the O–H···N and C–H···O intermolecular hydrogen bonds

The reason was indicated in the following description. To mark the weak C–H···O hydrogen bond which is defined H···O distance (d) of <2.80 Å and C–H···O angle (α) of over 90° [12, 13], one amphoteric molecule MeO composed of the supramolecular main-chains were interplayed by eight kinds of weak C–H···O hydrogen bonds between carboxy and ether oxygen atoms and carbon atoms neighboring on an electron-drawing pyridyl group and phenyl-methyl ether group as summarized in Table 1. In contrast to the Pr single crystal having two kinds of C–H···O hydrogen bonds, the MeO single crystal was stabilized by many C–H···O hydrogen bonds, which means the MeO single crystal composed of hydrogen bonded supramolecular network. As a result of X-ray structural analysis, the MeO single crystal was composed of antiparallel supramolecular main-chains stabilized

Table 1 Geometrical parameters D, d, α, and β of intermolecular hydrogen bonds

	D/Å	d/Å	α/°	β/°
O(3)–H···N(1)	2.61	1.53	171	–
C(1)–H···O(3)	3.45	2.52	158	117
C(5)–H···O(4)	3.23	2.54	126	120
C(12)–H(8)···O(1)	3.20	2.62	117	101
C(12)–H(9)···O(1)	3.48	2.68	137	125
C(12)–H(9)···O(2)	3.61	2.62	165	126
C(13)–H···O(4)	3.44	2.53	152	107
C(14)–H···O(4)	3.41	2.67	130	133
C(17)–H···O(4)	3.53	2.68	149	103

by O–H···N and C–H···O hydrogen bonds with high density crystal packing and network structure.

Structural transformation of the hydrogen-bonded supramolecular crystal of MeO

On 1st heating, two endothermic transitions were observed at 154 and 205°C as shown in Fig. 4. We determined transition enthalpy (ΔH) and entropy (ΔS) at each transition to discuss a thermal behavior. The transition enthalpy and entropy of the transition at 154°C were ΔH_1=4.1 kJ mol^{-1} and ΔS_1=9.60 J K^{-1} mol^{-1}, respectively. The transition at 205°C to isotropic liquid gave ΔH_2=65.2 kJ mol^{-1} and ΔS_2=136 J K^{-1} mol^{-1}. Both transitions were attributable to a thermo-reversible transition because the transition enthalpy at 205°C on heating was consistent with one at 182°C on cooling (ΔS= –136 J K^{-1} mol^{-1}). In the case of transition on heating at 154°C and cooling at 138°C, both of the transition entropies are identical (ΔS= ±9.60 J K^{-1} mol^{-1}). All transitions on 2nd heating and cooling were observed in the same manner. In the amphoteric molecule Pr having a propyl group recently reported by our proceeding [10], a reversible crystal phase transition was observed at 17°C with ΔH=1.0 kJ mol^{-1} and ΔS=4.44 J K^{-1} mol^{-1} and attributable to formation and cleavage of weak C–H···O hydrogen bond along the molecular short axis. In contrast, the first transition of the MeO single crystal having methoxy side-chain at 154°C gave significantly larger ΔH and ΔS than that of the Pr single crystal at 17°C, which means the transition at 154°C in the MeO single crystal was not simply change like the formation and cleavage of C–H···O hydrogen bonds along the molecular short axis.

What is a thermally induced structural transition at 154°C? To investigate the structural transformation, temperature-dependent XRD was measured. Figure 5 shows a temperature-dependency of XRD patterns at the range of 40–170°C of the MeO single crystal. The conformation of MeO was unalterable before 150°C, then after the first transition at 154°C, the crystal packing was transformed to different packing possessing the dominant periodic structures attributable to molecular long axis at 2θ=6.2°, half of the molecular long axis at 2θ=12.0°, supramolecular main chain at 2θ=15.5°, methylene chain at 2θ=21.0°, which values were similar to those of Pr [8]. This result indicates that the high density crystal packing of MeO shown in Fig. 3 transformed to similar crystal packing to low density crystal similar to Pr after the transition at 154°C. This behavior implies that the interplay between the side-chain methoxy groups in the high density MeO single crystal was disrupted by thermal energies, and then the similar crystal packing with low density to Pr-5 was formed immediately.

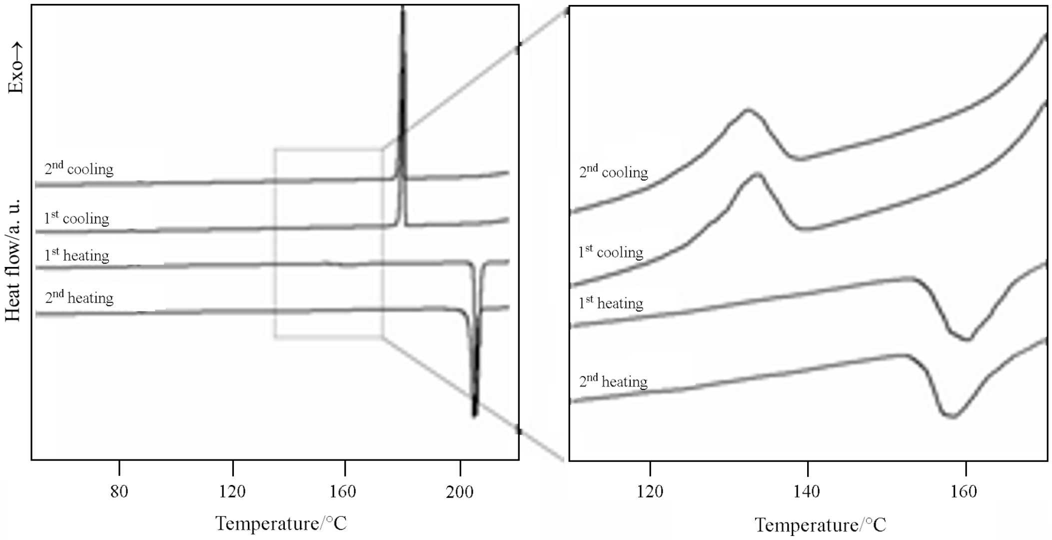

Fig. 4 DSC curves of MeO on heating and cooling at the rate of 10°C min^{-1}. Right column indicates the magnified curves in the range of 110–170°C

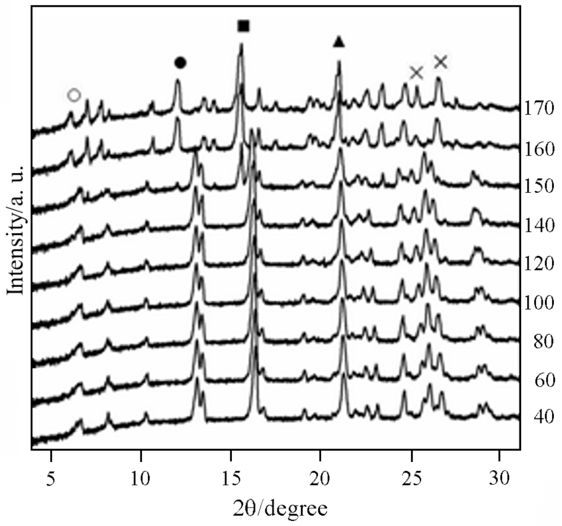

Fig. 5 Temperature-dependency of XRD patterns at 40–170°C of the MeO single crystal. The anticipated peaks after transition at 154°C of dominant periodic structures of ○ – molecular long axis, ● – half of the molecular long axis, ■ – supramolecular main chain, ▲ – methylene chain and × – pyridyl and phenyl layers are indicated

Conformation of the MeO crystal after transformed over 154°C

Macroscopic morphologies before and after transition at 154°C were unchanged by means of optical microscopic observations. And so we investigated atomic bond states in the MeO by thermally induced FTIR measurement to make clear the conformation of the MeO single crystal after transformation. Figure 6a presents simultaneous DSC-FTIR spectra of the MeO single crystal at the range of 2840–2970 $\mathrm{cm^{-1}}$ including peaks of methyl and methylene stretching vibrations. The methylene symmetric vibration with all-trans conformation ($\nu_{\mathrm{s.C-H}}$ (*t*)), methylene symmetric vibration with gauche conformation ($\nu_{\mathrm{s.C-H}}$ (*g*)), methylene asymmetric vibration with all-trans conformation ($\nu_{\mathrm{as.C-H}}$(*t*)) and methylene asymmetric vibration with gauche conformation ($\nu_{\mathrm{as.C-H}}$ (*g*)) of pentamethylene main chains were observed at 2860, 2870, 2920 and 2940 $\mathrm{cm^{-1}}$, respectively, and the methyl asymmetric vibration of the side-chain methoxy group ($\nu_{\mathrm{as.C-H}}$) was observed at 2950 $\mathrm{cm^{-1}}$.

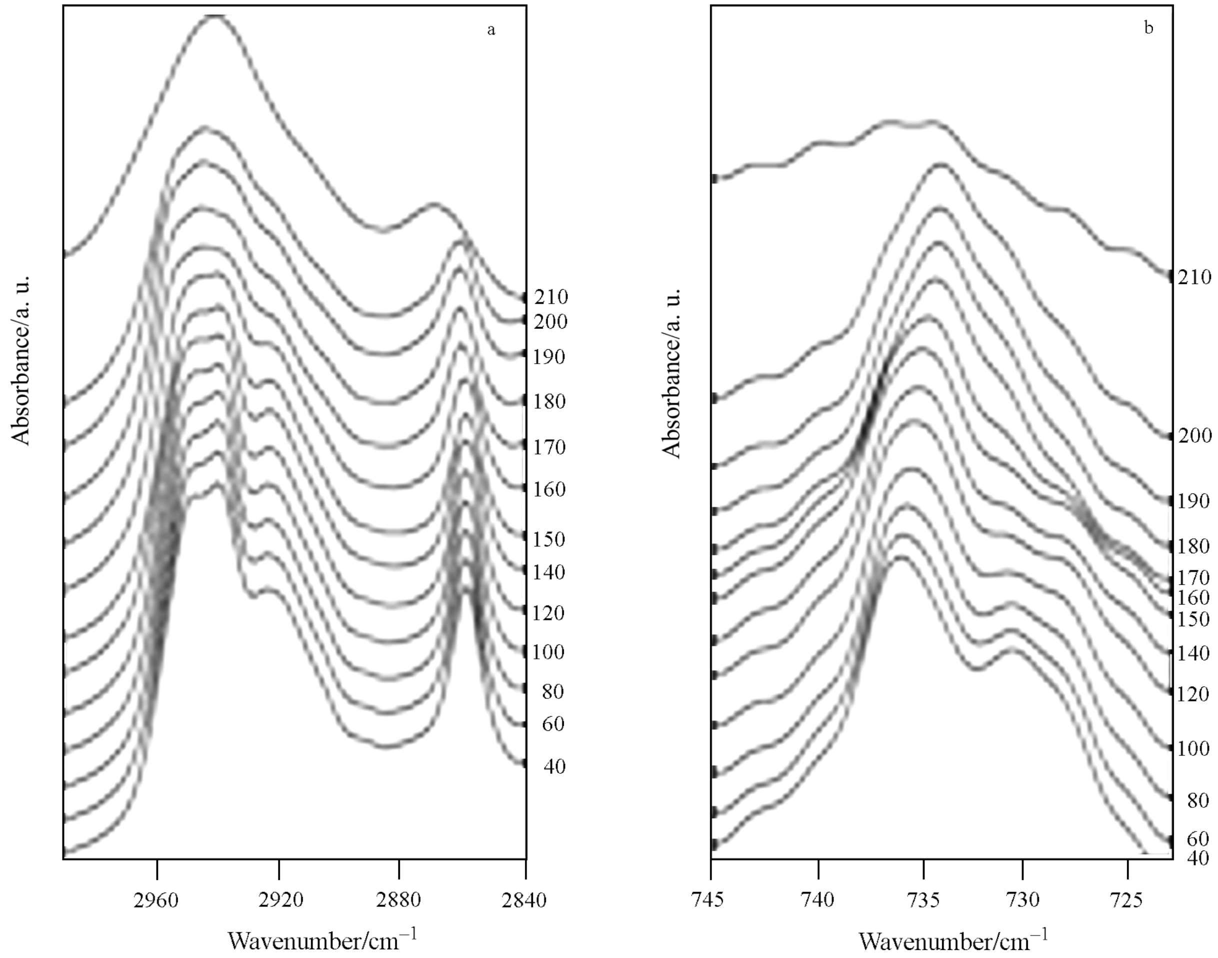

Fig. 6 Temperature-dependency of FTIR spectra of the MeO single crystal on heating in the range of a – 2840–2970 and b – 725–745 $\mathrm{cm^{-1}}$

After the transition at 154°C, the $\nu_{s.C–H}$ (*t*) and $\nu_{as.C–H}$ were high-wavenumber-shifted by increase of mobility of the side-chain methoxy group. This results supports the cleavage of C–H···O hydrogen bonds between the side-chain methoxy groups. In addition, the rocking vibrations ($\rho_{C–H}$) of the pentamethylene main chain attributable to 730 and 737 cm^{-1} were amazingly varied through the transition at 154°C as shown in Fig. 6b. The $\rho_{C–H}$ of as prepared MeO single crystal was split for two peaks, and then heating over 154°C the peaks became indistinctive as one peak at 735 cm^{-1}. This behavior was the same of a transition to a rotator phase of long chain *n*-alkanes [14, 15]. These simultaneous DSC-FTIR results prove that the pentamethylene main chain in the MeO single crystal transforms the all-trans conformation to the free-rotation conformation at 154°C on heating.

Thermally induced XRD and FTIR measurements of MeO single crystal demonstrated that the C–H···O hydrogen-bonded supramolecular network including the interplay between the side-chain methyl groups was cleaved at 154°C on heating by activization of the molecular motion of the methyl groups, and then the pentamethylene main chain also transformed the all-trans conformation (K1) to the free-rotation standing (K2) over the transition point of 154°C on heating. These reversible phase transitions of the MeO single crystal were summarized in Fig. 7. Thermophysical properties of the transition in the MeO single crystal at 154°C were ΔH= 4.1 kJ mol^{-1} and ΔS=9.60 J K^{-1} mol^{-1}, and larger than that of the structural transformation in the Pr single crystal at 17°C. These difference values were caused by changes of the conformation and the intermolecular interactions before and after the transition. We concluded that the weak C–H···O hydrogen bond with ΔH<10 kJ mol^{-1} [12, 13] enables to manipulate the intermolecular interaction in the crystal, and the relationship between the supramolecular network composed of the C–H···O hydrogen bond and the crystal packing have much effect on the thermal stability of the single crystal.

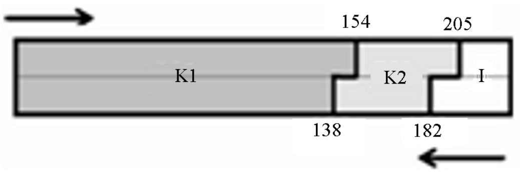

Fig. 7 Phase transition of the MeO single crystal

Conclusions

Herein we revealed the structural transformation of the hydrogen-bonded single crystal of MeO affected by thermal treatment. Two kinds of transitions which were from the K1-crystal with high density composed of all-trans pentamethylene main chain to the K2-crystal with low density composed of free-rotation pentamethylene main chain and side-chain methyl group at 154°C and from K2-crystal to isotropic liquid phase at 205°C were observed on 1st heating process. The transition at 154°C was related with not only formation and cleavage of the C–H···O hydrogen bonds between the molecular short axes similar to Pr [8], but also the conformational change from high-density-packed crystal to low-density-packed crystal. Such a C–H···O hydrogen bond attracts much attention since a suggestion of existence in DNA double helical structures [16]. We will try to investigate the detail conformational change related with the weak C–H···O hydrogen bond in other supramolecular architectures made of azopyridine carboxylic acids with a similar molecular structure.

References

1 J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim (1995).
2 F. Vögtle, Supramolecular Chemistry, John Wiley & Sons (1991).
3 K. Aoki, M. Nakagawa and K. Ichimura, Chem. Lett., (1999) 1205.
4 K. Aoki, M. Nakagawa and K. Ichimura, J. Am. Chem. Soc., 122 (2000) 10997.
5 M. Nakagawa, D. Ishii, K. Aoki, T. Seki and T. Iyoda, Adv. Mater., 17 (2005) 200.
6 D. Ishii, T. Yamada, M. Nakagawa, T. Iyoda and H. Yoshida, J. Therm. Anal. Cal., 81 (2005) 569.
7 D. Ishii, T. Yamada, M. Nakagawa, H. Yoshida and T. Iyoda, Trans. Mater. Res. Soc. Jpn., 30 (2005) 357.
8 D. Ishii, T. Yamada, T. Iyoda, H. Yoshida and M. Nakagawa, submitted for Chem. Lett., (2006).
9 D. Ishii, T. Yamada, T. Iyoda, H. Yoshida and M. Nakagawa, Proceeding of the 8th Polymers for Advanced Technologies International Symposium, (2005) 126.
10 H. Yoshida, R. Kinoshita and Y. Teramoto, Thermochim. Acta, 264 (1995) 173.
11 T. Steiner, Angew. Chem. Int. Ed., 41 (2002) 48.
12 G. R. Desiraju, Acc. Chem. Res., 29 (1996) 441.
13 T. Steiner, Chem. Commun., (1997) 727.
14 H. L. Casal, H. H. Mantsch and D. G. Cameron, J. Chem. Phys., 77 (1982) 2825.
15 V. Busico, A. Ferraro and M. Vacatello, J. Chem. Phys., 84 (1986) 471.
16 A. Asensio, N. Kobko and J. J. Dannenberg, J. Phys. Chem. A, 107 (2003) 6441.

PAT 2005

DOI: 10.1007/s10973-006-7893-7