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Thermal Studies on the Phase Transitions of *p*-*n*-Octadecyloxy Benzoic Acid (Part I)

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Thermal properties of *p*-*n*-octadecyloxybenzoic acid were investigated and the effects of the long paraffinic chain attached to the benzoic acid on the molecular motion in the mesophase are discussed. It was found that *p*-*n*-octadecyloxybenzoic acid had three crystalline forms; Crystal-I, Crystal-II and Crystal-III. Crystal-I is stable and Crystal-II and -III are metastable. It was concluded that the paraffinic chain in the Crystal-II and -III is frozen in a metastable state having conformations different from that of Crystal-I. It is suggested that *p*-*n*-alkoxybenzoic acids in general, has physical properties of both liquid and plastic crystals.

I INTRODUCTION

Thermal properties of a homologous series of *p*-*n*-alkoxybenzoic acid have long been studied. Many of them indicated that the compounds belong to the classification of liquid crystals. Jones *et al.*[1–3] found first from the examinations by polarized light that the homologous acids, from *p*-*n*-propoxy- to *p*-*n*-cetyloxybenzoic acids inclusive, transformed into milky liquid crystals with temperature. They suggested that the mesomorphism which occurred in the solids was due to the association of the acid in dimers. Further, according to their results, the homologous acids from *p*-*n*-heptyloxybenzoic acid onwards had relatively "monotropic phase" in the solid state, besides thermally stable crystal phase. Gray *et al.*[4] also reported previously that *p*-*n*-octadecyloxybenzoic acid had two phase transitions; the crystal–smectic phase and the smectic phase–isotropic liquid transitions. Herbert[5] calculated these transition enthalpies from calorimetric data. However, the thermodynamical rationale of the monotropic phase which is formed only in the solid state of *p*-*n*-alkoxybenzoic acids, from *p*-*n*-heptyloxybenzoic

acid onwards, by rapid cooling from the molten state, has not been clearly given.

The molecular motion in the mesophases of the homologous acids should be compared with that in the mesophase of *n*-alkyl metal carbonates, since both the acid and salt molecules consist of a rigid part, aromatic nucleus or metal, and a flexible paraffinic chain. Many studies[6–11] of the physical properties of the mesophases of *n*-alkyl metal carbonates have been reported. These results and the nuclear magnetic resonance spectra measured by Flautt *et al.*[12] indicate that the paraffinic chain in the mesophase identified as "subwaxy phase" is probably a smectic phase which has a chain conformation similar to that in the liquid state of the *n*-paraffins or *n*-alkylcarboxylic acids.[13] Only the aliphatic part moves violently in the mesophase. From the author's calorimetric measurements, it is confirmed that a rapid cooling from the mesophase produces a monotropic phase in the solid state. Therefore, in the case of the homologous acids from *p-n*-heptyloxybenzoic acid onwards, it was expected that such a motion of a flexible paraffinic chain would occur in the smectic phase and that a monotropic phase in the solid would be formed by rapid cooling.

Sadagami *et al.*[14] carried out polarization microscopic observations of *p-n*-octadecyloxybenzoic acid and suggested that the form of this smectic phase was analogous to that of smectic C which was proposed by Sackmann *et al.*[15] The form[16] of smectic C is considered to be related to the intramolecular structure entailing a gausche form with respect to the paraffinic chain conformation which is in the *trans* form in the crystal.[17] A rapid cooling from the smectic C phase may offer a monotropic phase in which the paraffinic chain forms a structure containing partially the gausche form.

In the present study, thermal properties of *p-n*-octadecyloxybenzoic acid were investigated and the motion of the paraffinic chains in the mesophase is discussed.

II EXPERIMENTAL

A Preparation

p-n-Octadecyloxybenzoic acid was previously synthesized by Dave *et al.*[18] Their method, which used *p*-hydroxybenzoic acid and an alkyl iodide or bromide for the preparation of *p-n*-octadecyloxybenzoic acid, gave a poor yield. So the following method which gave a better yield was adopted. 1.0 mole of *p*-hydroxymethyl benzoate was dissolved in 200 ml of dimethyl formamide. 1.2 moles of solid sodium were added to the solution. This mixture was refluxed for five to six hours with stirring at 150°C with careful attention to the water contamination. To the refluxed solution, 1.1 moles of

octadecyl bromide was added and the mixture was refluxed for seven hours with stirring at 150°C. The methyl ester of the alkoxy acid separated out. This ester was filtered and dissolved in 2 : 1 mixed solution of methylethylketone and ethyl alcohol continuing 1.2 moles of potassium hydroxide. This solution was refluxed for five hours at 75°C and finally treated with hydrochloric acid. *p-n*-Octadecyloxybenzoic acid was formed. This powder was filtered and recrystallized from toluene. The yield was about 75%.

The crystal obtained was identified as *p-n*-octadecyloxybenzoic acid by the use of NMR and IR measurements. The data from gas chromatography indicated the existence of impurities of about 0.2 wt. %, such as the homologous alkoxybenzoic acids.

B Thermal analysis

The samples used for the thermal experiments were recrystallized from toluene solution and dried under high vacuum at room temperature for 24 hours. Thermal analysis were carried out by using a Perkin–Elmer differential scanning calorimeter (DSC) model-II with samples of about 2 mg over the temperature range of 300 K to 420 K. The heat capacity of *p-n*-octadecyloxybenzoic acid was obtained from DSC curves in comparison to that of a single sheet of amorphous alumina. The values established by Furukawa[19] were taken as the standard. A sensitivity of 2 mcal/sec and a heating rate of 2.5 K/min were used in all measurements of heat capacity. The error in the heat capacity was found to be about 5% based on repeated experiments. About 7 mg of the sample was prepared in a pellet so as to avoid thermal hysteresis caused by the delay of thermal conduction.

C Polarization microscopy

All microscopic observations were made using a Leitz polarizing microscope. The liquid crystal specimens which were heated on a heating block mounted on a rotating stage were placed between crossed polarizers. A color plate ($\lambda = 540$ mμ) was used as a test plate to determine interference colors. The temperature of the sample was measured using a thermometer which can measure the difference of ± 0.5°K.

D X-ray diffraction

Samples used for the measurements were deposited on a TAC film base and diffraction patterns were obtained at room temperature by using a Rigaku Denki DC-1 X-ray diffractometer.

III RESULTS AND DISCUSSIONS

Figure 1 shows some DSC thermograms of *p-n*-octadecyloxybenzoic acid over the temperature range of 300 K to 420 K. As the temperature increases the thermogram of the recrystallized sample involves two endothermic transitions, one of which was the standard crystal–smectic phase transition and the other the smectic phase–isotropic liquid transition, as is shown in Run. 1. During cooling (Run. 2), the transformation from isotropic liquid to the smectic phase was observed even with rapid cooling as fast as 160 K/min. However, an exotherm considered as the transition from the smectic phase to crystal state appeared at 361 K, which was about 20 K lower than the stable crystal–smectic phase transition temperature, even with slow cooling at the rate of 0.32 K/min. This difference is so large that it can't be thermal hysteresis. Run. 3 and Run. 4 are heating thermograms of samples which were cooled from the isotropic liquid to 300 K by slow and rapid cooling rates, respectively. The exotherm observed at 355 K is probably attributed to a metastable–stable crystal transition, because the heating thermogram (Run. 5) of the sample annealed at 360 K identified with Run. 1.

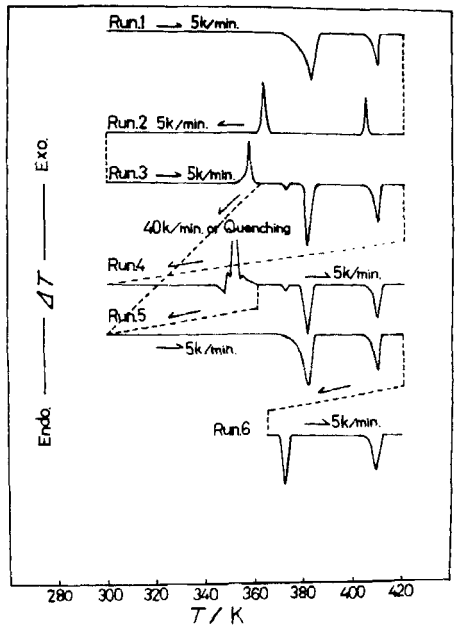


FIGURE 1 DSC thermograms of *p-n*-octadecyloxybenzoic acid. (heating and cooling rates are indicated on each curve)

In order to clarify the small endotherm in Run. 3 or Run. 4 in the vicinity of 372 K, the heating thermogram (Run. 6) of the sample, which was cooled from isotropic liquid to 366 K by a slow cooling rate and annealed at the same temperature for 20 min, was taken. The stable crystal–smectic phase transition was not obtained, but an endotherm was observed at 372 K. Since the enthalpy of the endotherm is about two-thirds of that of the phase transition, this transition is probably a metastable crystal–smectic phase transition. After the exothermic transition was accomplished, the solid state may be mixed with the metastable and stable crystals. Therefore, the appearance of this transition in Run. 3 or Run. 4 is reasonable. As is shown in Run. 4, a small endotherm was observed immediately before the exotherm at 355 K only when the sample was treated with a rapid cooling from the smectic phase or isotropic liquid. In order to check whether the endotherm is a glass transition, the quenched sample was annealed at 342 K where the endotherm was initiated. The extent of the endotherm depended on the annealing time at 342 K, as is seen in Figure 2. With increasing annealing time, the extent of the endotherm decreases gradually. This phenomenon differs from enthalpy relaxation[20] generally found on curves of annealed substances just below their glass transition temperatures. But, this is probably the same as the metastable solid–liquid transition, which has been recently

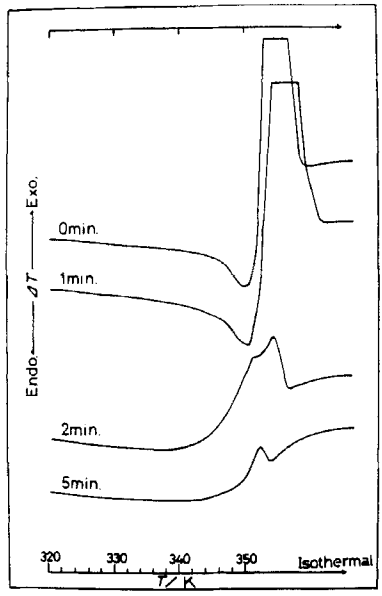


FIGURE 2 DSC thermograms of the samples which were cooled from the mesophase to 342 K at the rate of 160 K/min and annealed for 0, 1, 2 and 5 min, respectively.

reported in ethanol and cyclohexane by Seki and Suga.[21,22] Since such an endotherm was not observed when the sample was cooled slowly (Run. 3), there seems to be two metastable solids in addition to one stable crystal.

Measurements by x-ray diffraction were carried out to examine whether such metastable solids are crystalline or amorphous. The results are shown in Figure 3. The x-ray diffraction patterns of these two metastable solids exhibited sharp peaks like crystals. The diffraction patterns of the two are similar except for the pattern of the metastable solid formed by rapid cooling is somewhat broader. Both of these patterns were different from that of the stable crystal. In the discussions that follow, the stable crystal, the metastable crystal formed by cooling at a rate slower than 5 K/min and the metastable crystal formed by a rapid cooling faster than 40 K/min, will be abbreviated as crystal-I, crystal-II and crystal-III, respectively.

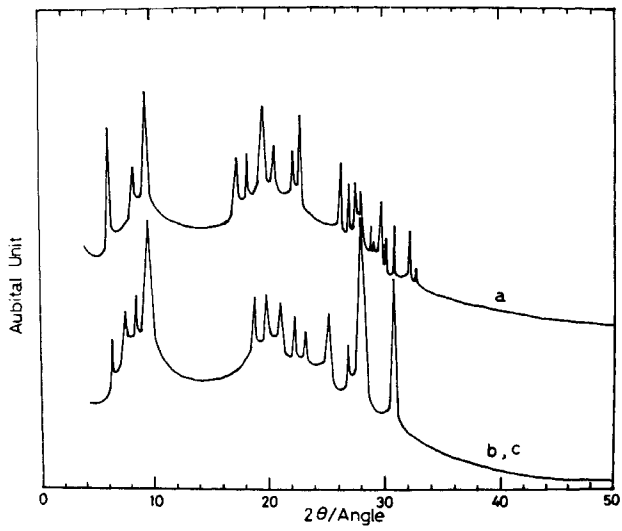


FIGURE 3 X-ray diffraction patterns of (a) crystal-I, (b) crystal-II and (c) crystal-III.

We tried to measure the heat capacity of *p-n*-octadecyloxybenzoic acid by using DSC in an effort to account for the thermodynamic relations among the solids. The values of the heat capacity involved an error of about 5% because all these experiments were carried out under isothermal experimental conditions but not adiabatic ones. Figure 4 shows the heat capacities of some samples in the temperature range of 320 K to 420 K. Thermodynamic relations among solids investigated by heat capacity measurements satisfy the above interpretation obtained from a set of DSC measurements.

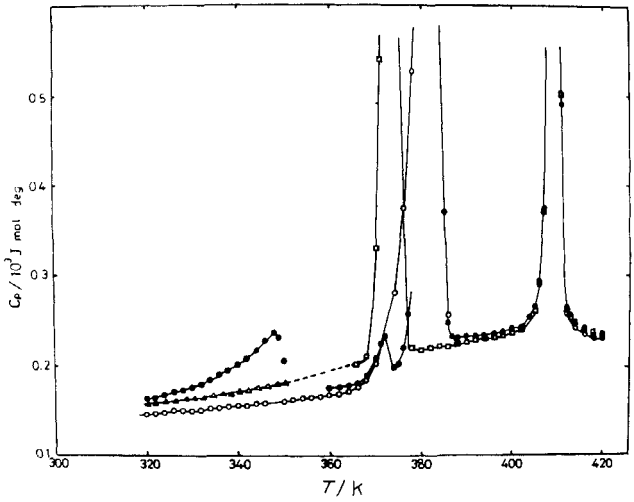


FIGURE 4 Heat capacities of the annealed samples of *p-n*-octadecyloxybenzoic acid. ○: crystal-I, △: crystal-II, ●: crystal-III and □: the sample (crystal-II) cooled from the mesophase to 365 K.

With increasing temperature, the heat capacity of crystal-III abnormally increased from 342 K, and then abruptly decreased up to the heat capacity of the crystal-I in the vicinity of 360 K. The transition at 342 K is the crystal-III–smectic phase transition. As is shown in the heat capacity of the crystal-II, at 372 K the crystal-II transforms into the smectic phase. It was proven that the heat capacity after the transition follows the line obtained by extrapolation of the smectic phase obtained in the case of crystal-I. It is meaningful to know transitions among solids in view of Gibb's free energy–temperature relation. Figure 5 presents this relation. When the smectic phase was cooled rapidly, the crystal-III phase appeared in the solid state. On the other hand, when it was cooled slowly, crystal-II was formed.

Table I gives the values of heat capacity drawn in Figure 4 and Table II offers thermal quantities of *p-n*-octadecyloxybenzoic acid.

In order to discuss the mechanism of phase transitions of *p-n*-octadecyloxybenzoic acid its structure must be known. Cell constants and space groups were found by Bryan[23] from single-crystal x-ray photographs for the members of the homologous series of *p-n*-alkoxybenzoic acids. He suggested that the acids from *p-n*-heptyloxybenzoic acid onwards were evidently closely related in structure and packing in the triclinic crystal system, and that this relationship could be extended up to at least *p-n*-octadecyloxybenzoic acid. At the same time, he inferred that as the alkyl chain increased in size, the aliphatic chain became the dominating structural feature and

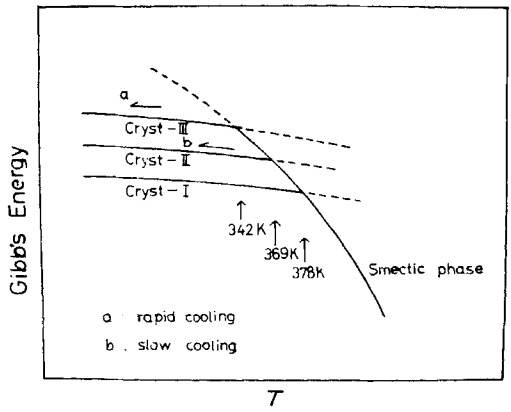


FIGURE 5 The illustrative curve of Gibb's free energy *versus* temperature.

TABLE I

The values of heat capacities of *p-n*-octadecyloxybenzoic acid given in Figure 4

Temperature K	C_p(crystal-I) KJ K^{-1} mol^{-1}	C_p(crystal-II) KJ K^{-1} mol^{-1}	C_p(crystal-III) KJ K^{-1} mol^{-1}
320	0.145	0.158	0.164
322	0.147	0.159	0.166
324	0.148	0.161	0.170
326	0.151	0.162	0.173
328	0.150	0.163	0.175
330	0.150	0.164	0.177
332	0.152	0.165	0.181
334	0.153	0.166	0.185
336	0.154	0.168	0.191
338	0.155	0.169	0.196
340	0.156	0.170	0.202
342	0.156	0.172	0.208
344	0.159	1.173	—
346	0.159	0.173	—
348	0.160	0.174	—
350	0.162	0.177	—
352	0.163	0.179	—
354	0.165	0.181	—
356	0.166	—	—
358	0.167	—	—
360	0.169	—	—
362	0.170	—	—
364	0.173	—	—
366	0.178	0.202	—
368	0.190	0.212	—
370	0.204	—	—
372	0.234	—	—

TABLE II

The transition enthalpies and the transition temperatures of *p-n*-octadecyloxybenzoic acid.

Transition	Transition Temperature K	Transition Enthalpies KJ mol^{-1}
crystal-I-smectic phase	379.5	67.3 ± 1.3
crystal-II-smectic phase	371.0	38.9 ± 0.7
crystal-III-smectic phase	342.5	–
smectic phase-iso. liquid	408.5	13.3 ± 0.3

their properties as represented by cell constants approached those of long-chain normal fatty acids.[24] Therefore, it is believed that the paraffinic chain controls the movements caused by heat in the smectic phase of *p-n*-octadecyl-oxybenzoic acid as well as the movements of paraffinic chain in the mesophase of *n*-alkyl metal carbonates.[25] In the case of *n*-alkyl metal carbonates, the layer structure is kept through dipole–dipole interactions among —COOM groups (M : metal atom) in the mesophase (particularly subwaxy phase). On the other hand, the paraffinic chain in the phase exists in a kind of motion similar to the liquid state.[12] The smectic phase of *p-n*-octadecyloxybenzoic acid may consist of a kind of schlieren texture named as smectic C,[14] which is formed by interactions between the aromatic rings instead of the dipole–dipole interactions described for *n*-alkyl metal carbonates. If it is assumed that the conformation of the paraffinic chain in the smectic phase is analogous to that of *n*-alkyl metal carbonates, the appearance of two kinds of crystalline metastable forms produced by various cooling rates of the mesophase will not be particularly surprising. So to speak, when the acid is cooled from the smectic phase, the paraffinic chain in the phase may remain unchanged and be frozen in as the metastable crystals. The following results of polarization microscopy support such considerations.

Figure 6 shows some photographs taken by a polarizing microscope equipped with a hot-stage. Figure 6a indicates that the molecular orientation in crystal-I is quite regular. As the temperature is increased, a kind of schlieren texture appeared, as shown in Figure 6b. This is the smectic C phase. A rapid cooling of this phase gave Figure 6c, in which a disordered state of the molecular arrangement is probably responsible for the paraffinic chains appearance. Based on the thermal results discussed previously, this state is assigned as crystal-III. The photograph Figure 6d presents the crystal-II obtained by slow cooling of the smectic phase. Like the pattern of the crystal-III, the molecular arrangement in that state is also disordered. Figure 6e shows a picture, which is essentially the same as Figure 6d, but this photograph is one after the crystal-II–crystal-I transition during the

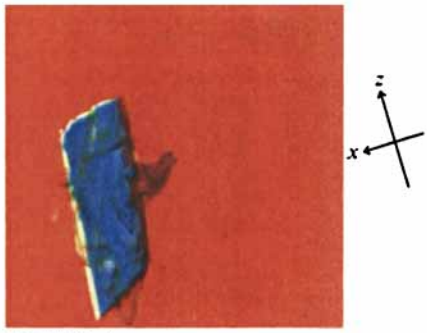


FIGURE 6a

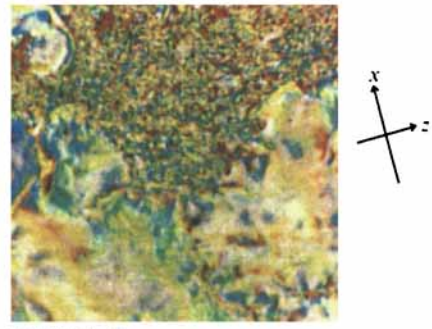


FIGURE 6b

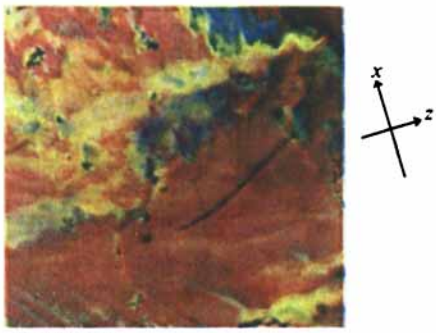


FIGURE 6c

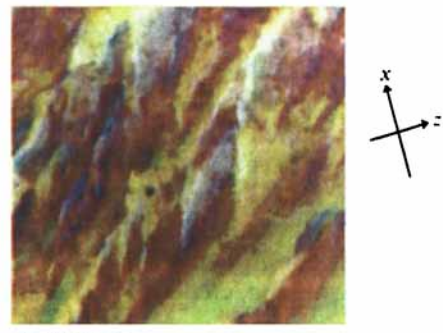


FIGURE 6d

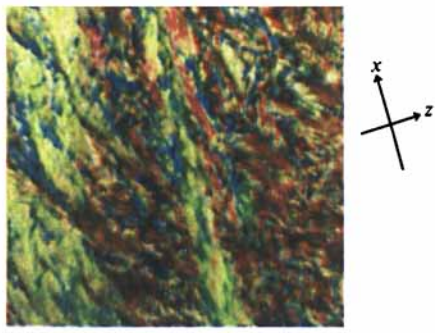


FIGURE 6e

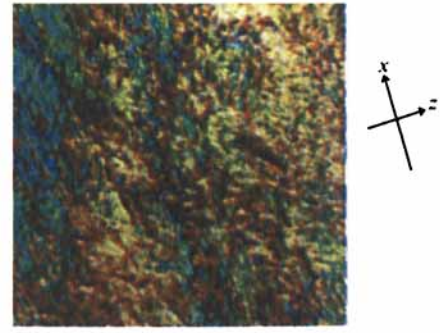
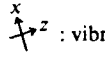


FIGURE 6f



: vibration direction of the sensitive color plate

FIGURE 6 Polarizing microscopic photographs (a): crystal-I at 20°C (× 1500), (b): smectic phase at 103°C (× 200), (c): crystal-III at 20°C (× 200), (d): crystal-II at 26°C (× 200), (e): solid-state at 85°C above crystal-II-crystal-I exothermic transition temperature (× 200) and (f): smectic phase the same as (a) (× 200).

crystal-II heating. The photograph shows that a small amount of the crystal-II remains in the solid state after the transition. This was not observed in the case when the sample was annealed for a long time at a temperature above the transition temperature. Also, this result qualitatively supports the idea of the existence of a transition at 372 K in Run. 3 and Run. 4 of Fig. 1. Further, with increasing temperature, the smectic phase occurred, as is shown in Figure 6f. The crystal-III–smectic phase transition was obscure under the microscope, because of the subsequent crystal-III–crystal-I exothermic transition. The existence of two different metastable crystals in addition to the stable crystal was confirmed by the polarizing microscope.

The fact that the homologous acids beginning with *p-n*-heptyloxybenzoic acid onwards with a long paraffinic chain in the molecule have individually one or more monotropic phases can be attributed to the flexibility of the chain, so that the chain conformation in the mesophase is easily frozen in by a cooling of the mesophase.

Results of infra-red spectroscopy which support the above suggestion will be published soon elsewhere.

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