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Thermal Studies on the Phase Transitions of p-n-Dodecyloxy and p-n-Tetradecyloxy Benzoic Acids.: (Part III)

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Thermal Studies on the Phase Transitions of *p*-*n*-Dodecyloxy and *p*-*n*-Tetradecyloxy Benzoic Acids.

(Part III)†

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Thermal properties of *p*-*n*-dodecyloxy and *p*-*n*-tetradecyloxy benzoic acids have been investigated using a differential scanning calorimeter. Heat capacities of thermally stable and metastable crystals of these acids were estimated and the effects of the paraffinic chain attached to the benzoic acid on the formation of a metastable crystalline state are discussed. It is suggested that the disorder of hydrogen bond configuration in associating carboxylic acids in pairs brings about the formation of a metastable crystal state for the alkoxy benzoic acids in general. Under the same conditions the mobile paraffinic chains control the modification of the hydrogen bond during the course of crystallization.

INTRODUCTION

The authors previously reported that *p*-*n*-octadecycloxy benzoic acid had metastable crystalline states which were alterable by the heat-treatment.[1] The results of calorimetry and infrared absorption spectroscopy of this acid and the deuterized one[2] suggested that the disorder of the hydrogen bond configuration involved in crystalline state had brought about the metastable crystalline state. At the same time, it is most probable that the regular

† This paper follows Part I presented in *Mol. Cryst. Liquid Cryst.*, **33**, 201 (1976) and Part II in *Mol. Cryst. Liq. Cryst.*, **39**, 109 (1977).

rearrangement of the crystal should be disturbed by the long paraffinic chains when the dimer-like associating molecules are frozen in the solid state.

In the consideration of the formation of metastable crystals of the *p-n*-alkoxy benzoic acids, the effect of the length of the paraffin chain on the crystallization process is of interest. Herbert[3] has made a phase transition map of this series of compounds up to the carbon number of 18. However, he did not draw attention to the mesomorphism of these acids. Paraffinic chain lengths of 12 and 14 are situated in the boundary region in the phase transition map where the nematic phase gives way to the smectic phase. In this paper, we have evaluated the thermodynamic data on *p-n*-dodecyloxy and *p-n*-tetradecyloxy benzoic acids to make a comparison with *p-n*-octadecyloxy benzoic acid.

EXPERIMENTAL

Preparation

The samples of *p-n*-dodecyloxy benzoic acid and *p-n*-tetradecyloxy benzoic acid were prepared by the same method as reported previously.[1]

Apparatus

A Perkin-Elmer DSC Model II Calorimeter equipped with a calculator system was used to evaluate the heat capacities. The error in the heat capacity was found to be about 4%.

RESULTS AND DISCUSSION

Figure 1 shows the phase transition map of the alkoxy benzoic acids. The transition temperatures gathered from several authors are cited together, thus, the accuracy of the values may differ from each other. From this figure, it is evident that *p-n*-dodecyloxy benzoic acid has two mesophases and *p-n*-tetradecyloxy benzoic acid lies at the boundary region where the nematic phase vanishes.

Figure 2 shows some DSC thermograms of *p-n*-dodecylocy benzoic acid over the temperature range 320 K to 430 K. As the temperature increases, the thermogram of the sample recrystallized from toluene solution exhibits three endothermic transitions, one of which is the standard crystal-nematic phase transition and the others the smectic–nematic and nematic–isotropic

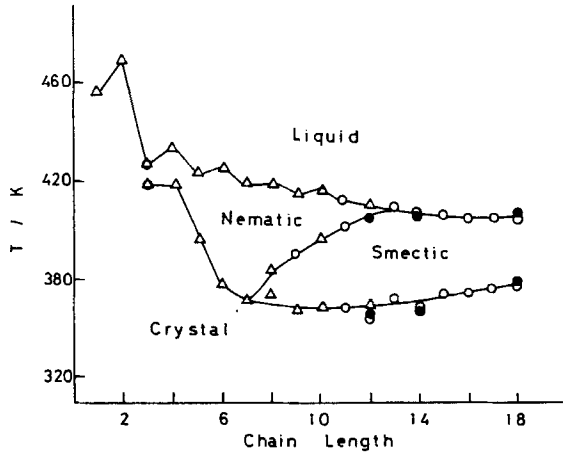

FIGURE 1 Phase transition map of *p-n*-alkoxy benzoic acids. △ Gray and Jones (Ref. 4); ○ Herbert (Ref. 3); ● this work.

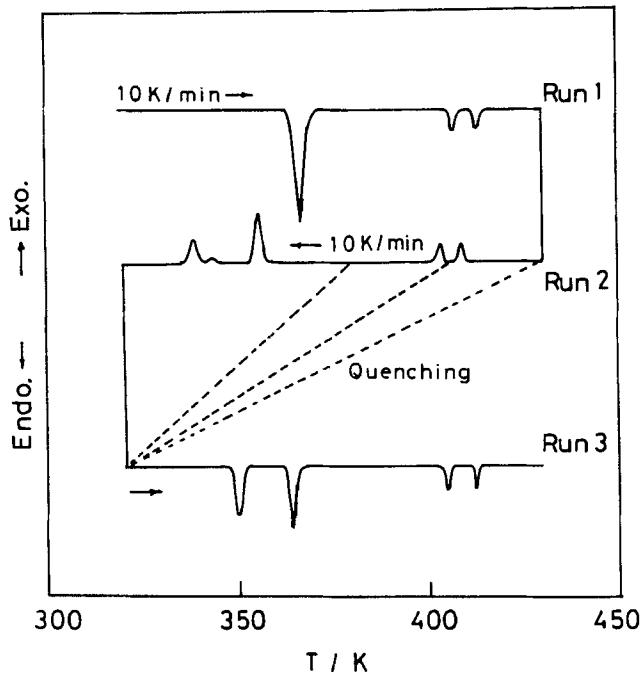

FIGURE 2 DSC thermograms of *p-n*-dodecyloxy benzoic acid (heating and cooling rates are indicated on each curve).

liquid phase transitions respectively (see Run 1). During cooling (Run 2), the transformation from isotropic liquid to the nematic phase and nematic to the smectic phase were observed at the same temperatures as in the heating thermogram. On the other hand, two exotherms appeared at the temperature region of smectic-crystal transition. The exotherm observed at 357 K was considered as the transition from smectic phase to the stable crystalline state. The other exotherm at 338 K was seen at about 30 K lower than the stable crystal–smectic phase transition. These transitions could be observed in the heating thermogram of a sample which had been cooled from the isotropic liquid to 320 K at 10 K/min (see Run 3).

In order to clarify the two endotherms at 350 K and 364 K in Run 3, heating thermograms were taken of the samples cooled from the smectic phase to 320 K or from nematic phase to 320 K with a rapid cooling rate. These thermograms were identical to that of Run 3 and no variation in the transition temperature was observed. It is clear from these thermograms that the temperature of lower transition is about 30 K lower than the crystal smectic phase transition temperature in Run 1, and the enthalpy of the transition is two-fifths of that of higher transition. Attempts to make a pure crystal without the higher melting peak were not successful. It was found that a preparation containing only the higher transition temperature phase could be obtained by long annealing after a very slow cooling (0.31 K/min) from the isotropic liquid.

Figure 3 shows the DSC thermograms of *p-n*-tetradecyloxy benzoic acid over the temperature range from 320 K to 430 K. Heating thermograms of a solution grown sample (Run 1) show two endothermic transitions which are standard crystal–smectic and the smectic–isotropic liquid phase transitions. The nematic phase was not found in *p-n*-tetradecyloxy benzoic acid. In the cooling thermogram, two exotherms of crystallization were observed (Run 2). On reheating these transitions appeared in a narrow temperature region (see Run 3). Rapid cooling from the isotropic liquid to 320 K or from the smectic phase to 320 K results in a similar pattern of thermograms as Run 3. If the sample was heated immediately after the quenching, gradual endothermic deviation in the base-line was observed over the temperature range of 320 K to 350 K. Unfortunately, this is not clear in the reduced drawings of Figure 3. The anomalous base-line shift can be seen under magnification as shown in Figure 4. The base-line became flat by increasing the annealing time at 320 K. Annealing for 2 hours at 320 K (VI) was sufficient to restore the original base-line (I).

Remarkably, similar phenomena were noted in samples annealed at a temperature higher than 320 K. For instance, on the thermogram of the sample which was cooled rapidly from the isotropic liquid phase to 350 K and reheated immediately an endotherm appears (Run 4 in Figure 3).

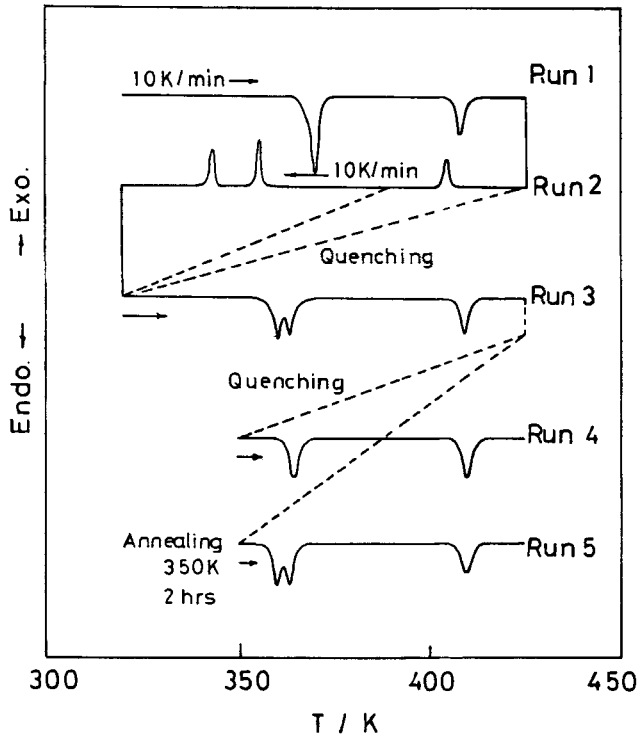

FIGURE 3 DSC thermograms of *p-n*-tetradecyloxy benzoic acid.

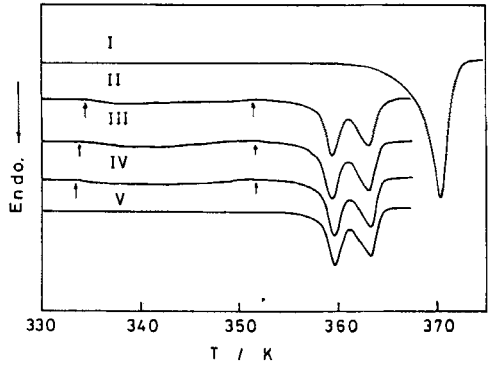

FIGURE 4 Enlarged DSC thermograms from 330 K to 380 K of *p-n*-tetradecyloxy benzoic acid. Recrystallized (I), immediately after quenching (II), kept at 320 K for 20 min (III), kept at 320 K for 1 hr (IV) and kept at 320 K for 2 hrs (V).

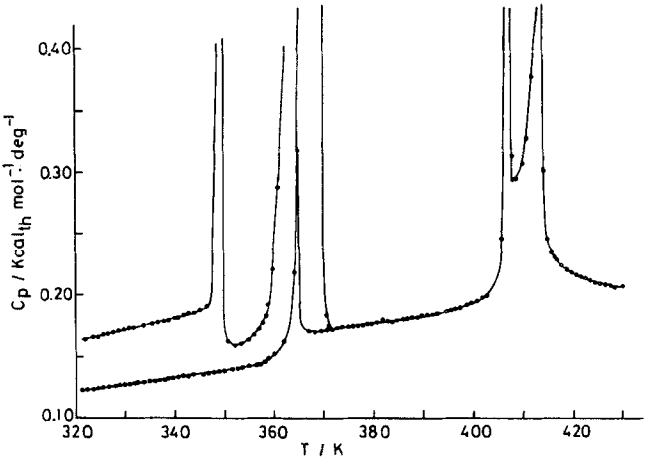

FIGURE 5 Heat capacities of *p-n*-dodecylocy benzoic acid. ○ Recrystallized from toluene solution (Crystal (I)). ● Quenched from the isotropic liquid phase to 320 K (Crystal (II)).

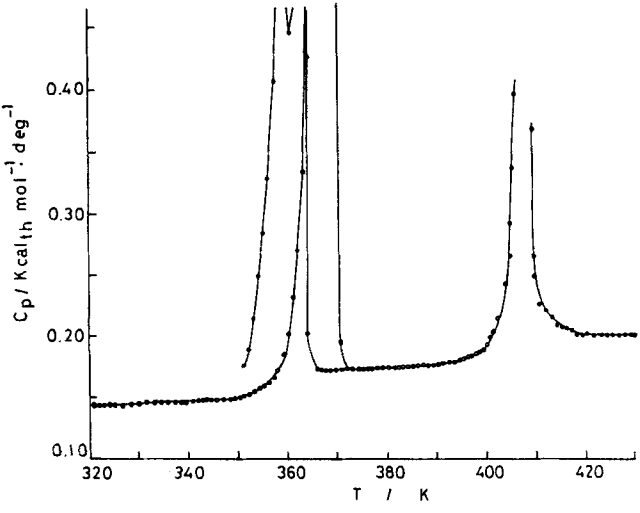

FIGURE 6 Heat capacities of *p-n*-tetradecyloxy benzoic acid. ○ Recrystallized from toluene solution (Crystal (I)). ● Quenched from the isotropic liquid phase to 320 K (Crystal (II)).

However, if the sample was held at 350 K for 2 hours, two endotherms appeared, see Run 5. These results suggested that various kinds of molecular configuration were frozen in the solid state immediately after quenching.

Heat capacities of *p-n*-dodecyloxy benzoic acid and *p-n*-tetradecyloxy benzoic acid were estimated for two different types of crystals; crystals prepared by rapid cooling from toluene solution (Crystal (I)); and crystals prepared by rapid cooling from 430 K (isotropic liquid) to 320 K (Crystal (II)). The results are shown in Figure 5 and Table I for *p-n*-dodecyloxy benzoic acid and also in Figure 6 and Table II for *p-n*-tetradecyloxy benzoic acid, respectively. It is apparent that the heat capacity of the Crystal (II) of *p-n*-dodecyloxy benzoic acid is higher than that of Crystal (I). The heat capacity of Crystal (II) of *p-n*-tetradecyloxy benzoic acid is not shown over the temperature range from 320 K to 350 K, in Figure 6, since they were scattered owing to the thermal histories of samples, as mentioned in Figure 4.

TABLE I

Heat capacity values for *p-n*-dodecyloxy benzoic acid

	C_p(I)	C_p(II)		C_p(I)	C_p(II)
Temperature K	$Kcal_{th}\ mol^{-1}\ K^{-1}$		Temperature K	$Kcal_{th}\ mol^{-1}\ K^{-1}$	
322.0	0.1226	0.1626	377.7	0.1745	0.1734
324.0	0.1235	0.1650	379.7	0.1764	0.1753
326.0	0.1249	0.1678	381.7	0.1784	0.1776
328.0	0.1259	0.1697	383.7	0.1768	0.1766
330.0	0.1273	0.1711	385.7	0.1793	0.1784
331.9	0.1282	0.1730	387.7	0.1802	0.1798
333.9	0.1292	0.1743	389.7	0.1826	0.1816
335.9	0.1301	0.1762	391.7	0.1830	0.1830
337.9	0.1306	0.1771	393.7	0.1840	0.1839
339.9	0.1330	0.1799	395.7	0.1874	0.1872
341.0	0.1349	0.1833	397.7	0.1893	0.1996
343.9	0.1349	0.1851	399.7	0.1937	0.1939
345.9	0.1358	0.1880	401.6	0.1937	0.1939
347.9	0.1372	0.2471	403.6	0.2045	0.2056
349.9	0.1392	0.2253	405.6	0.2444	0.2326
351.9	0.1396	0.1580	407.6	0.3135	0.3218
353.9	0.1410	0.1609	409.6	0.3070	0.3074
355.8	0.1425	0.1672	411.6	0.3765	0.3715
357.8	0.1449	0.1774	413.6	0.3000	0.3107
359.8	0.1552	0.2188	415.6	0.2343	0.2360
361.8	0.1611	0.4966	417.6	0.2229	0.2236
363.8	0.2277	1.9475	419.6	0.2174	0.2185
365.8	1.0745	0.1721	421.6	0.2139	0.2145
367.8	3.7915	0.1690	423.5	0.2094	0.2104
369.8	0.2601	0.1704	425.5	0.2084	0.2088
371.8	0.1727	0.1713	427.5	0.2064	0.2072
373.8	0.1731	0.1722	429.5	0.2063	0.2076
375.8	0.1741	0.1730			

TABLE II

Heat capacity values for *p-n*-tetradecyloxy benzoic acid

Temperature K	C_p(I) Kcal$_{th}$ mol^{-1} K^{-1}	C_p(II) Kcal$_{th}$ mol^{-1} K^{-1}	Temperature K	C_p(I) Kcal$_{th}$ mol^{-1} K^{-1}	C_p(II) Kcal$_{th}$ mol^{-1} K^{-1}
322.0	0.1410	—	377.7	0.1715	0.1743
324.0	0.1413	—	379.7	0.1718	0.1744
326.0	0.1427	—	381.7	0.1720	0.1767
328.0	0.1430	—	383.7	0.1756	0.1768
330.0	0.1432	—	385.7	0.1759	0.1769
331.9	0.1424	—	387.7	0.1772	0.1791
333.9	0.1427	—	389.7	0.1742	0.1760
335.9	0.1441	—	391.7	0.1756	0.1771
337.9	0.1410	—	393.7	0.1791	0.1804
339.9	0.1424	—	395.7	0.1805	0.1816
341.9	0.1438	—	397.7	0.1829	0.1839
343.9	0.1452	—	399.7	0.1908	0.1915
345.9	0.1476	—	401.6	0.1987	0.1981
347.9	0.1479	—	403.6	0.2402	0.2265
349.9	0.1481	0.1754	405.6	0.3947	0.3362
351.9	0.1517	0.1885	407.6	0.8219	0.8153
353.9	0.1541	0.2473	409.6	0.2476	0.2647
355.8	0.1598	0.3288	411.6	0.2196	0.2203
357.8	0.1720	0.5559	413.6	0.2079	0.2071
359.8	0.2027	0.4452	415.6	0.2038	0.2063
361.8	0.2703	0.9493	417.6	0.1987	0.1999
363.8	0.4227	0.2020	419.6	0.2000	0.2010
365.8	0.7083	0.1728	421.6	0.1992	0.2000
367.8	1.8526	0.1707	423.5	0.1973	0.1980
369.8	1.7095	0.1729	425.5	0.1976	0.1969
371.8	0.1718	0.1730	427.5	0.1990	0.1981
373.8	0.1709	0.1731	429.5	0.2003	0.1982
375.8	0.1701	0.1743			

Transitions among crystals having different histories are illustrated in terms of the Gibb's free energy temperature relationship in Figure 7. The results obtained from thermal analysis are explained on the curves of above figure, i.e. the transition temperature of Crystal (I) is always higher than that of Crystal (II), moreover, the quenched sample of *p-n*-dodecyloxy benzoic acid (Crystal (II)) is transformed to Crystal (I) by annealing. These results lead to us believe that the Crystal (II) is a metastable crystal. Accordingly, the lower melting peak in thermograms of Figures 2 and 3 is attributed to the transition from the metastable crystal to the smectic phase.

The transition temperatures and calculated transition enthalpies are listed in Table III along with previously reported results for *p-n*-octadecyloxy benzoic acid.[1]

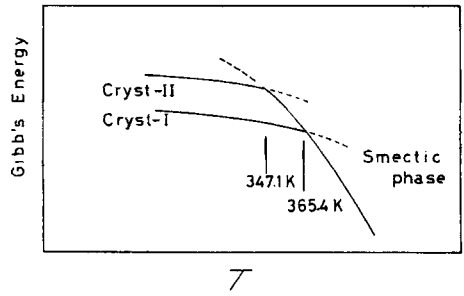

FIGURE 7 An illustrative curve of Gibb's free energy versus temperature for *p-n*-dodecyloxy benzoic acid.

We have suggested that the modified hydrogen bonds of carboxyl groups associated in pairs were frozen in metastable crystalline states.[1,2] Since the crystallization processes are considered to be controlled by the paraffinic chain attached to aromatic rings, the modified hydrogen bond should be rearranged during the crystallization if the paraffinic chain is not sufficiently long. The retardation effect may be increased by increasing the length of chain. Thus, it is reasonable to propose that the sample having a long paraffinic chain, such as *p-n*-octadecyloxy benzoic acid should show several kinds of metastable states. Also, the crystal-crystal transformation occurred easily in the time scale of the measurement.[1,2]

The above thermodynamic data indicates that the retardation effect is insufficient to make homogeneous metastable crystalline states in the cases of *p-n*-dodecyloxy and *p-n*-tetradecyloxy benzoic acids. This is confirmed by the fact that the enthalpy of transition from metastable to the smectic phase is

TABLE III

The transition temperature and the transition enthalpies of *p-n*-dodecyloxy, *p-n*-tetradecyloxy, *p-n*-octadecyloxy benzoic acids

Sample	Transition	Transition Temperature K	Transition Enthalpy KJ mol^{-1}
p-n-Dodecyloxy benzoic acid	Stable crystal–smectic phase	365.4	35.6
	Metastable crystal–smectic phase	347.1	3.6
	Smectic–nematic phase	405.3	1.8
	Nematic–isotropic liquid	411.6	2.0
p-n-Tetradecyloxy benzoic acid	Stable crystal–smectic phase	366.2	35.4
	Smectic–isotropic liquid	405.5	7.6
p-n-Octadecyloxy benzoic acid	Stable crystal–smectic phase	379.5	67.3
	Metastable crystal–smectic phase	371.0	38.9
	Smectic–isotropic liquid	408.5	13.3

smaller than that of *p-n*-octadecyloxy benzoic acid. From the time dependency of heat capacities in the solid state of *p-n*-tetradecyloxy benzoic acid, it is suggested that this compound is situated in the chain length boundary region among alkoxy benzoic acids where the influence of paraffinic chain remarkably appears. It may be concluded that the disorder of hydrogen bond configuration in the molecular arrangement results in metastable crystals of alkoxy benzoic acids. At the same time, mobile paraffinic chains control the modification of hydrogen bond in the course of crystallization.

References

1. M. Ikeda and T. Hatakeyama, *Mol. Cryst. Liq. Cryst.*, **33**, 201 (1976). (Note that in Table I and Figure 4 in this paper, the dimension of heat capacity; KJ mol^{-1} deg^{-1} should be replaced to $Kcal_{th}$ mol^{-1} deg^{-1}.)
2. M. Ikeda and T. Hatakeyama, *Mol. Cryst. Liq. Cryst.*, **39**, 109 (1977). (Note that in Table I and Figure 2 in this paper, the dimension of heat capacity; KJ mol^{-1} deg^{-1} should be replaced to $Kcal_{th}$ mol^{-1} deg^{-1}.)
3. A. J. Herbert, *Trans. Faraday Soc.*, **63**, 555 (1967).
4. G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179 (1953).