Successive Phase Transitions in Crystalline State of Mesogenic Butyl 4-[2-(Perfluorooctyl)ethoxy]benzoate

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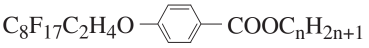
(Received August 17, 2004; CL-040973)

Successive phase transitions have been found in crystalline state of the title compound by X-ray diffractometry with synchrotron radiation and by adiabatic calorimetry. The transitions are at 173.5 and 174.2 K with a total entropy change of 7.26 $\mathrm{J\,K^{-1}\,mol^{-1}}$. The phase transitions are associated with a change of the periodicity of lateral molecular stacking in the monoclinic lattices with the common *b* axis, $Z = 4$, 16, and 12, for high, intermediate and low temperature phases, respectively.

Various kinds of fluorinated compounds have been synthesized to produce highly functional and/or new types of liquid crystalline materials.[1–3] Systematic changes of crystal structure were found and discussed in relation to the mesophase behavior and intermolecular interactions for alkyl 4-[2-(perfluorooctyl)-ethoxy]benzoates: separate packings of perfluoroalkyl (R_f) and alkyl (R_h) chains for members of shorter ($n = 2$) and longer ($n = 11$) chain lengths with monotropic smectic A (S_A) phase, while alternate packings of R_f and R_h chains for those of middle chain lengths ($n = 6$, 7) without S_A phase.[4]



(F8-n)

The butyl homologue (abbr. **F8-4**) has different crystal structures at 100 and 200 K.[4] The low temperature (L) phase has a cell three times larger than that of the high temperature (H) phase both having a common *b* axis as shown in Figure 1. The repeating period along the core stacking in L phase becomes three times longer than that in H phase. In both phases the molecular conformations are essentially the same except for the degree of disorder in R_f chains. The packing modes are of an intermediate type between the separate and alternate types, which was regarded as the result from competitive intermolecular interactions. This letter reports the discovery of an intermediate (M) phase between H and L phases and the behavior of successive H–M–L phase transitions.

X-ray diffraction intensities were measured with synchrotron radiation ($\lambda = 0.3282$ Å) on a Weissenberg camera at the BL04B2 in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2003A0395-ND1-np) for a single crystal obtained from a dichloromethane solution by slow evaporation. The data were collected and processed as previously described.[5] The compound used for calorimetry was synthesized anew as previously described[6] and purified by repeated recrystallization from a methanol solution. The sample purity was determined to be 99.9 mol % by means of the fractional melting method carried out in adiabatic calorimetry. The experimental details will be described together with the details of the calorimetric results.[7] The thermal behavior of **F8-4** below room temperature was studied by DSC (Perkin-Elmer Pyris 1) for various samples mentioned below in order to relate the X-ray diffraction to the calorimetric results.

An X-ray diffraction study with the low divergent and highly brilliant beams of synchrotron radiation detected M phase around 160 K between H and L phases on cooling and heating runs, as shown in Table 1. The relationship between the unit cell of the three phases is shown in Figure 1. The repeating period of M phase becomes fourfold of H phase. The reflection intensities of $h + l =$ odd for *hkl* are systematically weak (1/3 of those for $h + l =$ even, on average), which indicates that the main periodicity of 2 is modified to 4. However, the detailed structure of M phase could not be determined because of low reflection intensities.

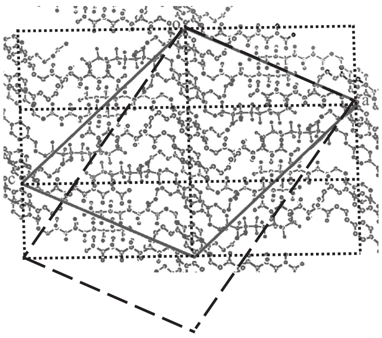


Figure 1. Relationship of the unit cells. The cells of H, L, and M phases are shown by ··········, ——(gray), and — —, respectively. The molecules shown are for L phase.

Figure 2 shows the heat capacity anomaly composed of double peaks at 173.5 and 174.2 K. The whole enthalpy and entropy changes are 1.26 $\mathrm{kJ\,mol^{-1}}$ and 7.26 $\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. The double peaks indicate the existence of an intermediate phase between the two, which is consistent with the result of X-ray diffraction. The anomaly observed the most clearly was the as-synthesized sample, and it became broader after melting. The closed circles in Figure 2 are those of the second run after melting.

In order to relate the double peaks of C_p to the unit cell changes, DSC measurements were performed on the powder specimen used for the C_p study (sample **1**) and single crystals used for X-ray study (sample **2**). The former gave a sharp double peak at 172–173 K, while the latter gave a broad peak around 165 K, both on cooling and heating, as shown in Figure 3. The melting temperature of the former was higher by 1 K than that of the latter, which indicates a slight difference in purity. Then,

Table 1. Lattice parameters of **F8-4** at various temperatures

T/K	200*	165	160 (cooling)	160 (heating)	150	100^a
Space Group	$P2_1/a$	$P2_1/a$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	10.863(2)	10.853(2)	26.516(1)	26.564(2)	26.553(17)	26.348(2)
b/Å	9.618(13)	9.619(3)	9.609(1)	9.621(1)	9.622(1)	9.5144(7)
c/Å	23.900(5)	24.075(8)	39.997(4)	40.053(5)	32.036(3)	31.673(2)
β/°	91.302(6)	91.431(11)	101.745(4)	101.786(6)	113.526(4)	113.657(10)
V/Å^3	2496.2(9)	2512.4(12)	9977.6(15)	10020.6(18)	7504(5)	7272.8(9)
Z	4	4	16	16	12	12
D_{calcd}/g cm^{-3}	1.704	1.694	1.706	1.698	1.700	1.754

^{a}The data were measured on RAPID (cited from Ref. 4).

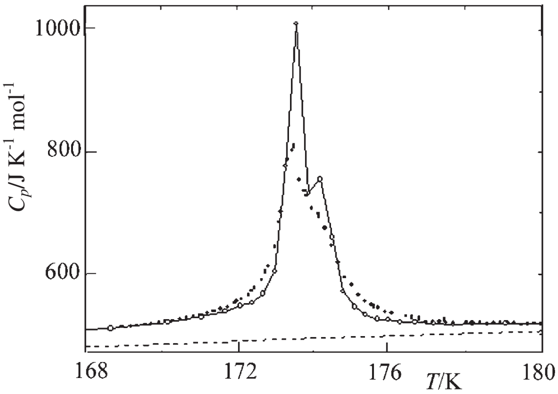


Figure 2. Molar heat capacities in the temperature region of the crystalline phase transitions. Open and closed circles are of the virgin sample and of melt/frozen sample, respectively. A broken line denotes the baseline to determine the transition enthalpy.

the crystalline phase transition temperatures were measured for the specimens obtained from a solution of mixtures of **1** and **2** with the ratio of 2:1 (**3**) and 1:2 (**4**). They showed intermediate behavior between **1** and **2**. The peak profile is broadened and the transition temperature decreases with decreasing the purity. The peak profiles show that the anomaly comprises two successive phase transitions for all the samples studied. Single crystals (**5**) crystallized from a solution of **1** gave a sharper double peak than the original specimen at the same temperature, which should be due to the better crystallinity.

In conclusion, a new crystalline phase (M) has been found between H and L phases in **F8-4**, which was confirmed by X-ray diffractometry and calorimetry. Two phase transitions in a very narrow temperature range (≈0.7 K) have been elucidated for the first time for organic crystals. It has been also found that the crystalline phase transitions are highly sensitive to the sample purity. Further detailed studies of calorimetry will be described elsewhere.[7]

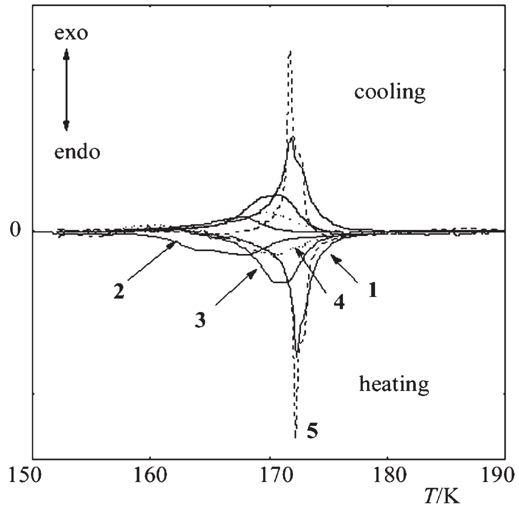


Figure 3. DSC traces of various samples **1**–**5** (see text).

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Published on the web (Advance View) November 6, 2004; DOI 10.1246/cl.2004.1566