316 *Bull. Chem. Soc. Jpn. Vol. 80, No. 2, 316–320 (2007)*

Calorimetric Study on Mesogenic Butyl 4-[2-(Perfluorooctyl)ethoxy]-benzoate. Successive Phase Transitions in the Crystalline State

Kayako Hori,*[1] Minako Maeda,[1] Atsusi Nidaira,[2] Hitoshi Kawaji,[2] and Tooru Atake[2]

[1]Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo 112-8610

[2]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503

Received July 20, 2006; E-mail: khori@cc.ocha.ac.jp

Thermodynamic studies have been made on the title compound in order to elucidate the successive phase transitions between low-temperature (**L**), intermediate-temperature (**M**), and high-temperature (**H**) crystalline phases, which were previously found by X-ray diffraction studies. Using homemade adiabatic calorimeters in the temperature range of 13–360 K, the transition temperatures of the **L**–**M** and **M**–**H** phase transitions were determined as 173.5 and 174.2 K, respectively, and the total entropy change due to the two phase transitions was 7 to 11 J K^{-1} mol^{-1}, depending on the assumed baseline. Melting from **H** phase to the isotropic liquid phase was at 341.18 K with an entropy change of 103 J K^{-1} mol^{-1}, while that from the super-cooled Sm A phase to the isotropic liquid phase was at 325.3 K with an entropy change of 11.5 J K^{-1} mol^{-1}. Thermodynamic functions $H(T)$–$H(0)$, $S(T)$–$S(0)$, and $(G(T)$–$G(0))/T$ were obtained for the first time for a perfluoroalkyl chain compound, except for unsubstituted perfluoroalkanes, and they are 122.4 kJ mol^{-1}, 851.0 J K^{-1} mol^{-1}, and 440.5 J K^{-1} mol^{-1}, respectively, at 295.15 K. The nature of the phase transitions is discussed in terms of an order–disorder type of mechanism.

Various kinds of fluorinated compounds have been synthesized in order to obtain highly functional and/or new types of liquid crystal materials.[1–3] In order to evaluate the effect of fluorination, we have carried out a crystallographic and computational studies on a series of simple compounds, alkyl 4-[2-(perfluorooctyl)ethoxy]benzoates (abbr. **F8-*n***),[4] which have a Smectic A (Sm A) phase, although monotropic, for shorter alkyl chain lengths ($n \leq 5$) and longer ones ($n \leq 11$) but not for middle ones.[5,6] A systematic change in crystal structures was found according to the chain length, as schematically shown in Fig. 1. The compounds with $n = 2$ and 11 have a separate type of molecular packing, in which the perfluoroalkyl (R_f) and alkyl (R_h) chains aggregate away from each other, while compounds with $n = 6$ and 7 have alternate type of packing, in which R_f and R_h chains aggregate in an alternating fashion. These features were closely related to the appearance of the mesophase.

The butyl homologue ($n = 4$, abbr. **F8-4**) has an intermediate type of packing, in which the butyl chain extends towards the R_f chain of a neighboring molecule, leading to the partial overlap of molecules. Different cell parameters were found at 100 K (low-temperature phase, **L**) and at 200 K (high-temperature phase, **H**). The repeating period along the core stacking in the **L** phase is three times as long as in the **H** phase. A temperature-variable X-ray diffraction study using synchrotron radiation in the SPring-8 revealed that a third phase existed between the **H** and **L** phases, which was designated as intermediate (**M**) phase.[7] The unit cell is four times larger than that of the **H** phase. Adiabatic calorimetry also confirmed the existence of the phase transitions.[7] The present paper gives a full description of the calorimetric studies carried out in the temperature range of 13–360 K in order to confirm and evaluate the thermodynamic properties of the compound for the first time as a thorough adiabatic calorimetry for a compound with a R_f chain, except for unsubstituted perfluoroalkanes.[8]

Experimental

Adiabatic Calorimetry. Compound **F8-4** was synthesized by previously described method,[5] and the sample was purified by repeated crystallization from methanol. Three runs of heat capacity measurements were carried out using different calorimeters ac-

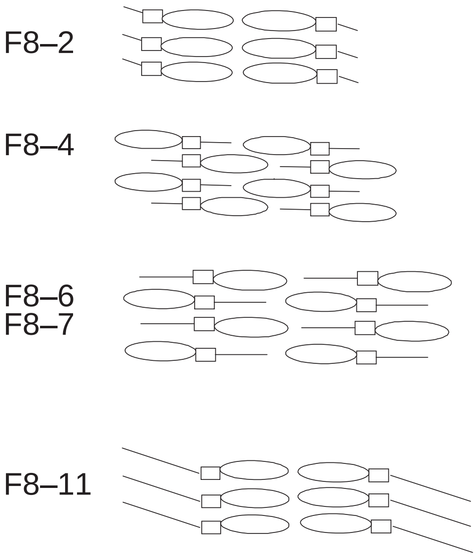

Fig. 1. Schematic diagram of packings of **F8-2**, **F8-4**, **F8-6**, **F8-7**, and **F8-11**. Ellipsoids, lines, and squares denote R_f chains, R_h chains, and core moieties, respectively. Cited from Ref. 4.

Published on the web February 13, 2007; doi:10.1246/bcsj.80.316

cording to the temperature range. First, the heat capacity (C_p) in the temperature range of 108–360 K was measured using a homemade adiabatic calorimeter[9] using 0.91551 g of as-synthesized sample. The purity and the triple point of the virtually pure sample were estimated to be 99.95 mol % and 341.20 K, respectively, from the fractional melting plots. In succession, the C_p around the crystalline phase transition region and at higher temperatures was measured. The C_p in the temperature range of 40–130 K was measured using a different adiabatic calorimeter;[10] 1.3297 g of another sample solidified from the melt was used. The working thermometers mounted on these two calorimeter vessels were platinum resistance thermometers (model S1059PJ5X6; Minco Products, Inc.) calibrated on the basis of the international temperature scale of 1990 (ITS-90). Finally, the C_p in the temperature range of 13–50 K was measured using a third adiabatic calorimeter;[11] for this measurements, 1.1096 g of the same sample from the previous run was used. In this calorimeter, the thermometer was an iron–rhodium resistance thermometer (model 5187U; Tinsley and Co., Ltd., UK) calibrated on the basis of ITS-90. The data of each run were consistent except for the C_p around the crystalline phase transition region.

DSC Measurements. Preliminary measurements and detailed analysis of the phase transitions including thermal hysteresis study were made by differential scanning calorimetry (DSC). For the low-temperature region, a power-compensated DSC (Perkin-Elmer Pyris 1) was used in the temperature range from 98 to 303 K. The amount of the sample used for the measurements was 7–9 mg. The temperature scanning rate was $10\,\mathrm{K\,min^{-1}}$. For the higher temperature measurements between 298 and 358 K, a heat-flux scanning DSC (Seiko DSC-22C) was used. The amount of the sample was 3–5 mg, and the heating and cooling rate was 2 and $-5\,\mathrm{K\,min^{-1}}$, respectively.

Results and Discussion

Crystalline Phase Transitions. The results of the C_p measurements of **F8-4** in the whole temperature range are shown in terms of the molar heat capacity in Fig. 2, where the crystalline phase transition at about 174 K (a in Fig. 2), the melting of **H** phase (b), and the melting of the supercooled Sm A (c) are clearly seen. The smoothed values of the C_p at rounded temperatures and some thermodynamic functions calculated from the present data are given in Table 1; the C_p below the lowest temperature measured (13 K) was estimated by smooth extrapolation from the high temperatures down to 0 K. No phase transition was found below the crystalline phase transition at about 174 K. On the other hand, the previous X-ray study[4] made at 100 and 200 K showed that two of the three crystallographically independent molecules have highly disordered R_f-chains even in the **L** phase (at 100 K). Thus, it is considered that the disordered structure in the **L** phase might be quenched at low temperatures or the ordering proceeds gradually with decreasing temperature below 100 K. However, no anomaly nor glass-transition phenomenon was observed in the C_p measurements.

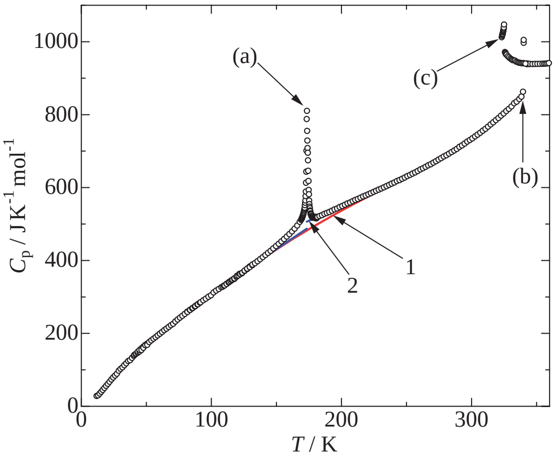

Fig. 2. Molar heat capacities of **F8-4** in the whole temperature region. (a) Crystalline phase transition, (b) melting of **H** to the isotropic liquid, and (c) melting of Sm A to the isotropic liquid. Two assumed baselines without a step (1) and with a step (2) are shown in red and blue, respectively.

From the C_p measurements on perfluoroalkanes, the contributions of CF_2 and CF_3 groups to C_p were presented as functions of temperature.[8] By using the data, the ratio of contributions of C_8F_{17}-moiety to the total C_p was estimated as shown in Fig. 3. The ratio is almost constant in the temperature range of 40–130 K and decreases in the temperature range of 140–210 K because of the total C_p increase due to the phase transitions. The ratio has a maximum value in 220–270 K and then again decreases due to the increase of C_p below the melting. However, the difference between the constant value in the temperature range (0.575) and the maximum value in the higher temperature range (0.560) is not significant; the change in the degree of disorder is not very different between the R_f chains and the other moiety both in the lower and higher temperature range. Thus, we speculate that the disorder in the **L** phase is quenched at low temperatures.

Figure 4 shows the C_p anomaly due to the phase transitions on an extended scale, where double peaks are clearly seen. Although the shape of the anomaly varies with the sample treatment, there are two peaks. Thus, the two phase transitions are at 173.5 and 174.2 K. The sample obtained from the melt shows a broad and truncated anomaly, but the asymmetric profile indicates that the peak comprises two portions. As it is difficult to separate the two anomalies, the enthalpy and entropy of transition were estimated in total. For the estimation of excess heat capacity two baselines were assumed as shown in Fig. 1. From the smooth baseline (1 in Fig. 2), the entropy change ($\Delta_{tr}S$) was calculated to be $11\,\mathrm{J\,K^{-1}\,mol^{-1}}$, while $7\,\mathrm{J\,K^{-1}\,mol^{-1}}$ was obtained from a different baseline (2 in Fig. 2). The results of the calculation are given in Table 2, where the values of the phase transitions for the samples before and after melting are in good agreement. The entropy change is attributable to a change of 1/3 of molecules from having ordered R_f chains in **L** to disordered R_f chains in **H**. The number of disordered configurations (W) is estimated to be 12 ($\approx 2^4$) and 53 ($\approx 2^6$) from $1/3R\ln W = \Delta_{tr}S$.

Melting Behavior. C_p of **F8-4** around the melting point is shown in Fig. 5, in which the melting of **H** phase and that of the super-cooled Sm A phase are clearly seen. The properties of melting, i.e., the temperature, enthalpy change, and entropy change, are summarized in Table 2.

The entropy of fusion of the **H** phase ($103\,\mathrm{J\,K^{-1}\,mol^{-1}}$) is attributed to the positional, rotational, and conformational dis-

Table 1. Thermodynamic Functions of **F8-4**

T/K	$C_p(T)$/J K^{-1} mol^{-1}	$S(T)$–$S(0)$/J K^{-1} mol^{-1}	$(H(T)$–$H(0))T^{-1}$/J K^{-1} mol^{-1}	$(G(T)$–$G(0))T^{-1}$/J K^{-1} mol^{-1}
15	38.5	29.8	16.0	13.9
20	59.8	43.8	24.3	19.6
30	100.7	76.0	43.0	32.9
40	136.9	110.0	62.1	47.9
50	168.9	144.0	80.3	63.7
60	198.1	177.5	97.5	79.9
70	225.8	210.1	113.9	96.2
80	254.2	242.1	129.6	112.4
90	281.1	273.6	145.0	128.6
100	306.6	304.5	159.9	144.6
110	331.6	334.9	174.4	160.6
120	357.1	364.9	188.5	176.3
130	383.3	394.5	202.5	192.0
140	411.1	423.9	216.4	207.5
150	439.9	453.2	230.3	222.9
160	472.0	482.6	244.4	238.2
phase transition				
190	532.3	573.3	289.2	284.1
200	548.5	601.0	301.8	299.2
210	564.7	628.2	313.9	314.2
220	580.6	654.8	325.7	329.1
230	596.5	681.0	337.1	343.9
240	612.8	706.7	348.2	358.4
250	629.9	732.0	359.2	372.9
260	648.1	757.1	369.9	387.2
270	667.0	781.9	380.6	401.3
280	687.5	806.5	391.2	415.4
290	709.5	831.0	401.8	429.3
298.15	728.8	851.0	410.4	440.5
300	733.4	855.5	412.4	443.1
310	759.7	880.0	423.2	456.8
320	788.7	904.5	434.1	470.4
330	820.6	929.3	445.4	483.9

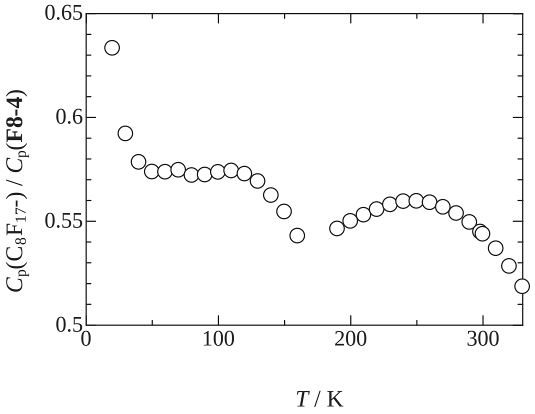

Fig. 3. Heat capacity ratio of R_f (C_8F_{17}-) to **F8-4**.

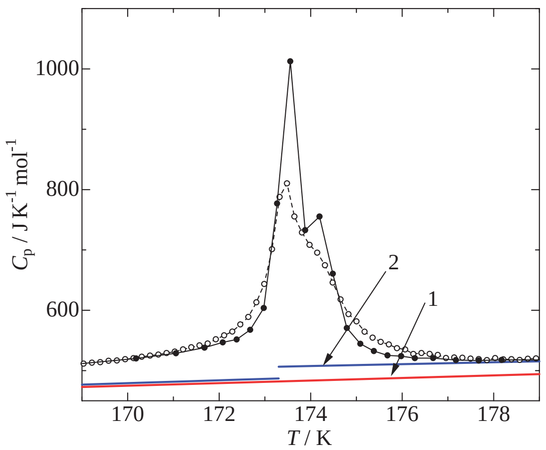

Fig. 4. Molar heat capacities of **F8-4** in the temperature region of the crystalline phase transition. Closed circles are for an as-prepared sample and open circles are for samples obtained from the melt. Two assumed baselines without a step (1) and with a step (2) are shown in red and blue, respectively. Adapted from Ref. 7.

ordering of the molecules. The contributions of the positional and rotational disorders for a rigid, non-spherical molecule were estimated to be 30–60 J K^{-1} mol^{-1}.[12] Similar values (55–65 J K^{-1} mol^{-1}) were obtained for the melting of a core moiety of a mesogen.[13] On the other hand, the contribution of a single bond for the chain melting was estimated to be 9.5 J K^{-1} mol^{-1} for macromolecules.[12] More precisely, the values were assigned to be 10.85 and 9.78 J K^{-1} mol^{-1} for even and odd chains, respectively.[14] From these values, we roughly estimated the number of single bonds responsible for the disordering

Table 2. Enthalpy Changes and Entropy Changes of the Phase Transitions and the Melting

Scheme of baseline	Without a step		With a step	
	$\Delta_{tr}H$/kJ mol^{-1}	$\Delta_{tr}S$/J K^{-1} mol^{-1}	$\Delta_{tr}H$/kJ mol^{-1}	$\Delta_{tr}S$/J K^{-1} mol^{-1}
Before-melting sample	1.97	11.2	1.15	6.9
After-melting sample	1.94	11.0	1.13	6.8
Sm A-isotropic liquid	3.75	11.5		
H-isotropic liquid	35.3	103		

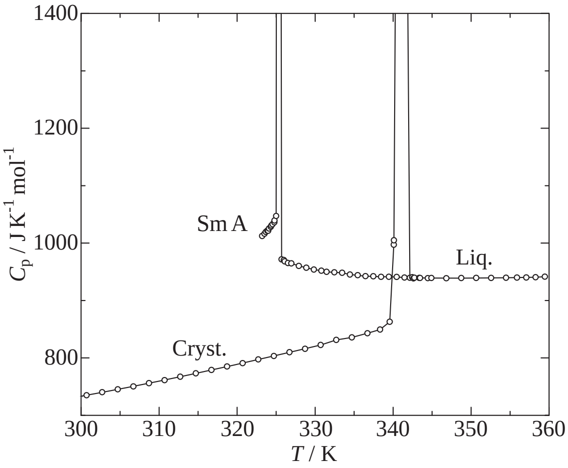

Fig. 5. The molar heat capacities of **F8-4** in the temperature region of meltings of **H** and Sm A phases to the isotropic liquid.

during fusion to be 4–7, which is comparable to the number of single bonds in a butyl and an ethoxy groups of the molecule. Thus, it is interpreted that the highly disordered R_f chains in the **H** phase does not contribute to the entropy of fusion.

The transition entropy of Sm A-isotropic liquid, 11.5 J K^{-1} mol^{-1}, is quite normal for this type transition.[15] The slope of C_p is slightly negative in the super-cooled liquid, while a sharp increase in C_p is observed just below the Sm A-isotropic liquid-phase transition. Samples obtained from the melt showed the same melting behavior as that of the as-synthesized sample.

The Nature of the Successive Phase Transitions in the Crystalline State. It is generally known that the crystalline phase transitions are highly sensitive to the sample purity. DSC measurements were performed on the powder sample used for the C_p study (designated as **1**), and on single crystals used for the X-ray study (designated as **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 Fig. 6. The melting temperature of the latter was lower by 1 K, indicating a slightly lower purity than that of the former. Crystalline phase transition temperatures were measured for the specimens, which were obtained by crystallization from a methanol solution of mixtures of the specimens **1** and **2** with ratios of 2:1 (**3**) and 1:2 (**4**). As shown in Fig. 6, they showed intermediate behavior. The peak profile broadened, and the peak interval widened as the purity decreased. From the peak profiles, it was confirmed that the anomaly comprises two successive phase transitions for all of the samples studied. The transition temperatures are roughly estimated as the apices of a trapezoid. The lowering of the melting temperature of 1 K corresponded to the lowering of the transition temperatures of 5 K (upper) and 8 K (lower) between the two extreme cases (**1** and **2**). It is concluded that the transitions are affected by impurities more seriously than fusion. Furthermore, the lowering of the lower-temperature transition is larger than the higher-temperature one, being interpreted that the more ordered **L** phase is affected more seriously by impurities than the less ordered **M** phase.

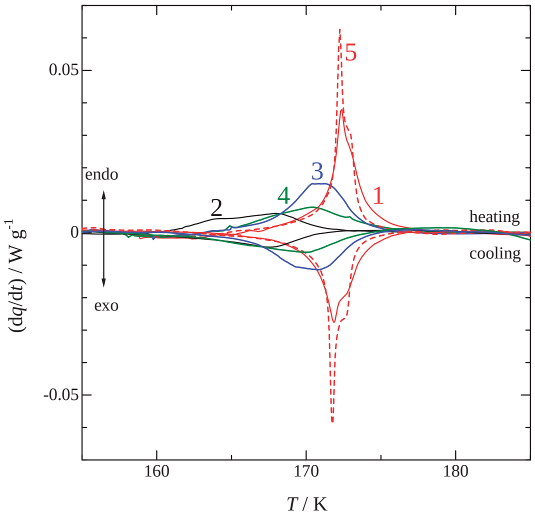

Fig. 6. DSC traces on heating (upper) and cooling (lower) for the specimen used for C_p study (**1**), single crystals used for X-ray diffraction study (**2**), the specimens obtained from a solution of a mixture of **1** and **2** in the ratio of 2:1 (**3**) and 1:2 (**4**), and single crystals from **1** (**5**). Adapted from Ref. 7.

On the other hand, single crystals that crystallized from a solution of **1** (designated as **5**) gave a sharper double peak than the original powder sample at almost the same peak temperatures. Samples obtained from a melt show broader profiles than the original sample, while the transition temperatures remain the same, which was mentioned in the previous section. These facts indicate that the reduction of the crystallinity promotes the pretransition phenomenon. However, the effect of physical purity (crystallinity) is not so significant as that of chemical purity.

Conclusion

For butyl 4-[2-(perfluorooctyl)ethoxy]benzoate, the heat capacity was measured using homemade adiabatic calorimeters in the temperature range of 13–360 K. Thermodynamic functions $H(T)–H(0)$, $S(T)–S(0)$, and $(G(T)–G(0))/T$ were obtained for the first time for a perfluoroalkyl-chain compound, except for perfluoroalkanes. Successive phase transitions in the crystalline state were elucidated, and they occur in a very narrow temperature range (0.7 K, peak-to-peak). With the DSC study, the transition behavior was revealed to be highly sensitive to impurities. Transition temperatures, enthalpy changes, and entropy changes were measured for the super-cooled Sm A to the isotropic and the high-temperature crystal phase to the isotropic phase transitions.

References

1 As a review: F. Guittard, E. T. de Givenchy, S. Geribaldi, A. Cambon, *J. Fluorine Chem.* **1999**, *100*, 85.

2 X. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume, C. Tschierske, *J. Am. Chem. Soc.* **2003**, *125*, 10977.

3 V. Percec, M. Glodde, G. Johansson, V. S. K. Balagurusamy, P. A. Heiney, *Angew. Chem., Int. Ed.* **2003**, *42*, 4338.

4 M. Yano, T. Taketsugu, K. Hori, H. Okamoto, S. Takenaka, *Chem. Eur. J.* **2004**, *10*, 3991.

5 H. Okamoto, H. Murai, S. Takenaka, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 3163.

6 M. Duan, H. Okamoto, V. F. Petrov, S. Takenaka, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2735.

7 M. Maeda, M. Nagasawa, M. Tachibana, H. Kawaji, T. Atake, A. Iida, T. Ozeki, K. Hori, *Chem. Lett.* **2004**, *33*, 1566.

8 Y. Jin, A. Boller, B. Wunderlich, B. V. Levedev, *Thermochim. Acta* **1994**, *234*, 103, and references cited therein.

9 Y. Moriya, H. Kawaji, T. Atake, unpublished.

10 A. Nidaira, H. Kawaji, T. Atake, unpublished.

11 T. Atake, H. Kawaji, A. Hamano, Y. Saito, *Rep. Res. Lab. Eng. Mater., Tokyo Inst. Technol.* **1990**, *15*, 13; T. Tanaka, T. Atake, H. Nakayama, T. Eguchi, K. Saito, I. Ikemoto, *J. Chem. Thermodyn.* **1994**, *26*, 1231.

12 B. Wunderlich, J. Grebwitcz, *Adv. Polym. Sci.* **1984**, *60/61*, 1.

13 G. W. Smith, *Mol. Cryst. Liq. Cryst.* **1979**, *49*, 207.

14 M. Sorai, K. Tsuji, H. Suga, S. Seki, *Mol. Cryst. Liq. Cryst.* **1980**, *59*, 33.

15 E. M. Barrall, II, J. F. Johnson, *Thermal Properties of Liquid Crystals, in Liquid Crystals and Plastic Crystals*, ed. by G. W. Gray, P. W. Winsor, John Wiley, Chichester, **1974**, Vol. 2, p. 254.