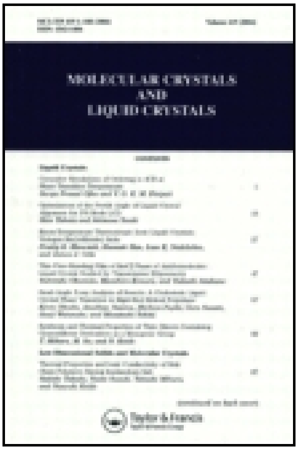

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Branching of the Perfluorinated Chain Influences the Liquid-Crystalline Properties of Semifluorinated Alkanes: Perfluorooctyl- and Perfluoroisononyl-n-Alkanes—a Comparative Study

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Branching of the Perfluorinated Chain Influences the Liquid-Crystalline Properties of Semifluorinated Alkanes: Perfluorooctyl- and Perfluoroisononyl-n-Alkanes— a Comparative Study

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Two series of semifluorinated-n-alkanes (SFAs) of comparable perfluorinated chain length but different terminal group constitution, namely perfluorooctyl-n-alkanes [F–$(CF_2)_8$–$(CH_2)_n$–H, in short F8Hn] and perfluoroisononyl-n-alkanes [$(CF_3)_2CF(CF_2)_6$–$(CH_2)_n$–H, in short iF9Hn] were synthesized. Their thermal properties were analyzed by means of differential scanning calorimetry (DSC), on both heating and cooling of the samples. The textures of the synthesized semifluorinated alkanes were investigated with the microscopy in polarized light. Similar to previously investigated perfluorodecyl-n-alkanes, perfluorooctyl-n-alkanes containing fewer than 12 methylene groups form smectic B phase. F8H8, F8H9, and F8H10 show a tendency to supercool and preserve smectic B ordering even below the transition temperature. For F8H11, the phase transition from smectic B to 3D crystal structure, manifesting itself as a rapid recrystallization, has been observed. Perfluorooctyl-n-alkanes of 12 or more methylene groups do not form liquid-crystalline phases. In contrast to perfluorooctyl-n-alkanes, perfluoroisononyl-n-alkanes are not capable of liquid-crystalline phase formation, regardless of the hydrogenated moiety length and the experimental conditions.

Keywords: differential scanning calorimetry; liquid-crystalline properties; semifluorinated alkanes

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1. INTRODUCTION

Normal alkanes and their perfluorinated analogs have different chemical and physical properties, which are reflected in their limited mixing, originally described by Scott [1]. Different properties of these molecules are due to significant differences between fluorine and hydrogen atoms in the electronegativity, polarity, and atomic radii. Namely, the atomic radius of fluorine is twice as large as that of hydrogen (72 pm and 37 pm, respectively) [2], whereas it is comparable with carbon (72 pm and 77 pm). This causes a different conformation of the hydrocarbon and the perfluorohydrocarbon chain. The former has a planar all-trans conformation, whereas the latter is helical, resulting from the steric hindrance [3]. Semifluorinated alkanes (SFAs) are very interesting diblock compounds, possessing both chains (i.e., a polymethylene chain and a perfluorinated hydrocarbon fragments) covalently bound within one molecule. They can be described by the general formula $F{-}(CF_2)_m{-}(CH_2)_n{-}H$, abbreviated as FmHn. They were first synthesized in the early sixties of the preceding century by Brace [4], and their properties, both in the solid state and in solution, were described for the first time by Rabolt *et al.* in 1984 [5]. The two different moieties of a SFA molecule have opposing character, namely the perfluorinated chain of a helical conformation is fluorophilic and oleophobic whereas the hydrogenated fragment of a flat all-trans conformation is fluorophobic and oleophilic. Because of such a diblock structure, SFAs behave like amphiphiles at the oleic/fluorous interface and are called *primitive surfactants* after Turberg and Brady [6]. Their surface activity, both in different organic solvents and in perfluorinated liquids, was investigated by Binks *et al.* [7,8] and Höpken *et al.* [9]. In 1991, Gaines [10] proved that some SFAs are capable of Langmuir monolayer formation and can be successfully deposited onto solid substrates with the Langmuir–Blodgett technique.

In 1985, Mahler *et al.* [11] reported that a representative of SFAs, namely perfluorodecyl-n-decane, abbreviated as F10H10, forms smectic liquid-crystalline phases, although its structure is not typically mesogenic because most of the mesogenic molecules have a rigid frame of biphenyl, azobenzene, cyclopentanoperhydrophenantrene, or other cyclic molecule, functionalized in axial positions with suitable substituents [12]. In the case of semifluorinated alkanes, liquid-crystalline-phase formation originates, similar to their surface activity, from their diblock structure and the rigidity of the perfluorinated moiety [13]. Liquid-crystalline phases of perfluorodecyl-n-alkanes were further investigated by Höpken *et al.* [9] and Viney *et al.* [14–16]. Upon texture analysis and X-ray measurements, the liquid-crystalline phases formed by perfluorodecyl-n-alkanes were classified as smectic B; however, in some cases higher ordering, such as smectic G or J, were also determined. In our previous paper [17], the influence of the length of the hydrogenated fragment on the liquid-crystalline properties of perfluorodecyl-n-alkanes was described. The present contribution deals with the liquid-crystalline properties of perfluorooctyl- and perfluoroisononyl-n-alkanes. The purpose of these investigations was to verify how the shortening of the perfluorinated chain by two CF_2 groups (as compared to perfluorodecyl-n-alkanes) affects the liquid-crystalline phase formation. The other objective was to verify whether the *iso*-branching in perfluorononyl-n-alkanes influences the ability to form the liquid-crystalline phase. To fulfill these aims, semifluorinated alkanes of these two homologous series were synthesized, and their liquid-crystalline and thermal properties were analyzed by means of polarizing microscopy and differential scanning calorimetry (DSC).

2. EXPERIMENTAL

2.1. Synthesis

The following compounds of the general formula $F{-}(CF_2)_8{-}(CH_2)_n{-}H$ (perfluorooctyl series) and $(CF_3)_2CF(CF_2)_6{-}(CH_2)_n{-}H$ (perfluoroisononyl series), where $n = 7$–16 and 8–16, respectively, were synthesized following the procedure described by Rabolt *et al.* [5]. Perfluorooctyl iodide (98%) was purchased from Aldrich and perfluoroisononyl iodide (98%) from Fluorochem. The respective n-alkenes (98–99%) were supplied by Aldrich. All the substrates were used as received, without further purification. Purity of the obtained semifluorinated alkanes (99%+) was checked by ^{1}H NMR, ^{13}C NMR, mass spectroscopy, and elemental analysis.

2.2. Thermal Analysis

2.2.1. Differential Scaning Calorimetry (DSC)

The DSC analysis was performed on a DSC 821e Mettler Toledo calorimeter. Specimens with mass of ca. 20–40 mg were scanned at $3^{\circ}\mathrm{min}^{-1}$. All samples were investigated in three heating/cooling cycles from -50 to 70°C. No dependence between the thermal history of the samples and the course of DSC curves was observed. An empty aluminum crucible was used as a reference. The temperatures of anomalies are given with the precision of 0.5°C and the enthalpy changes at the transitions with the precision of about 10%.

2.2.2. Optical Microscopy

Microscopic observations were performed on specimens held between thin circular glass cover slips, using a Biolar PI (PZO, Poland) polarizing microscope equipped with a Linkam (U.K.) THM 600 hot stage and TMS 90 temperature controller. The temperature range studied was from -50 to 70°C. Different heating and cooling rates within the range 0.2–30°min^{-1} were applied. During the phase transitions, the temperature was stabilized. The magnification was 500 times, and the results were observed by Hitachi CCD color video camera and digitalized.

3. RESULTS

To visualize the textures of the investigated semifluorinated alkanes, microscopic observations of the samples in the polarized light were applied. The resultant images for the selected representatives are presented in Fig. 1. For perfluorooctyl-n-alkanes with the methylene groups number $n = 8$–11, typical mosaic textures, characteristic for liquid-crystalline smectic phase B or higher smectics (such as G or J) are observed (Fig. 1a,b), whereas when $n > 11$, lamellar structures of three-dimensional (3D) crystals were seen (Fig. 1c,d).

To get further insight into phase transitions observed in the samples, differential scanning calorimetry (DSC) measurements were conducted for all the perfluorooctyl-n-alkanes, and the resultant DSC

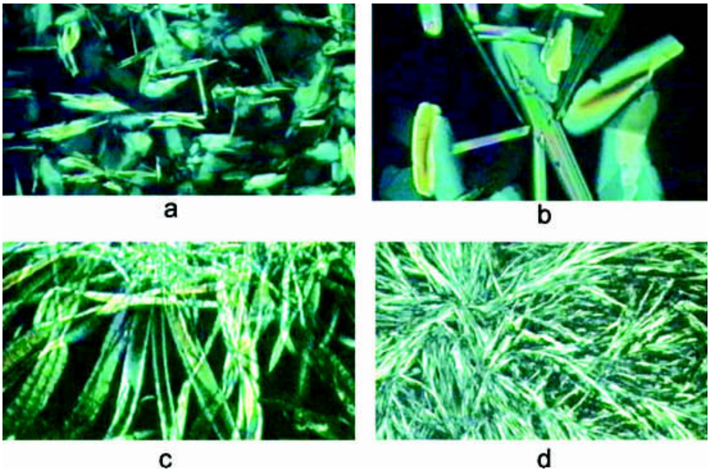

FIGURE 1 Textures of perfluorooctyl-n-alkanes: a) F8H8 (T = 15.6°C), b) F8H9 (T = 31.6°C), c) F8H12 (T = 33.0°C), d) F8H16 (T = 45.1°C).

curves, both upon heating of the samples (lower curves) and cooling (upper curves), are presented in Fig. 2. For clarity of presentation, the results were divided into three groups corresponding to SFAs: with short hydrogenated fragment, n = 8 and 9 (Fig. 2a); with hydrogenated moiety of intermediate length, n = 10–12 (Fig. 2b); and with long hydrogenated chain, n = 13–16 (Fig. 2c). The DSC curves for F8H8 and F8H9 (Fig. 2a) exhibit only one peak (both at heating and cooling) corresponding to the transition smectic ⟷ isotropic (lower curve) or

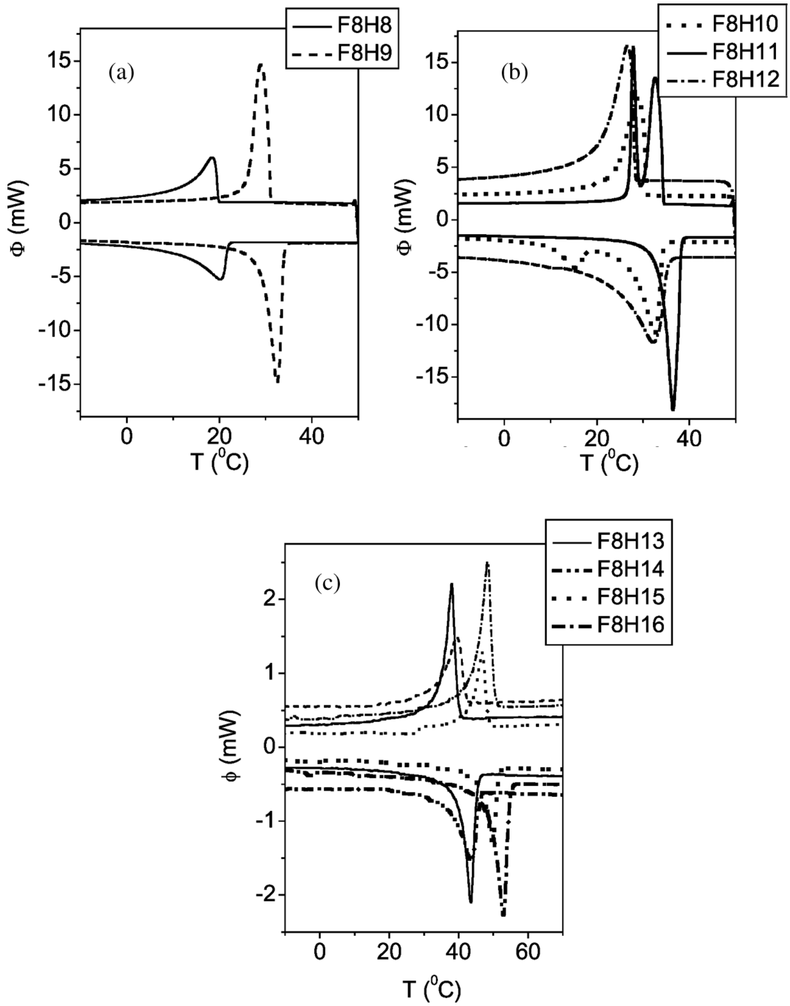

FIGURE 2 DSC curves for the investigated perfluorooctyl-n-alkanes.

isotropic ⟷ smectic phase (upper curve). Different behavior was observed for F8H10 and F8H11 (Fig. 2b). For F8H10, a peak corresponding to the transition smectic ⟷ isotropic appears at ca. 33°C, and an additional peak of lower intensity, corresponding to a phase transition smectic ⟷ crystalline, is clearly visible at ca. 15°C. The latter has not been detected in the course of the cooling curve. In contrast, in the course of heating DSC curve of F8H11, only one peak corresponding to the transition smectic ⟷ isotropic is observed, whereas on cooling two peaks are visible: one at higher temperature value corresponding to the transition isotropic ⟷ smectic and the second at lower temperature corresponding to smectic ⟷ crystalline transition. The DSC curves for F8H12 differ from those discussed previously because only one peak is visible, both on heating and cooling. The results for perfluorooctyl alkanes with $n > 12$ (Fig. 1c) are similar to F8H12, because only one peak, corresponding to melting (crystalline ⟷ isotropic) (heating curve) or freezing (isotropic ⟷ crystalline) (cooling curve), is observed.

From the DSC curves, enthalpies of phase transitions were calculated, and together with transition temperature values thus are gathered in Table 1. Generally, the phase-transition temperatures on heating of the investigated perfluorooctyl alkanes are 4–6°C higher than those noticed upon cooling. These temperatures increase with the number of methylene groups, and no odd–even effect is observed. As far as the ΔH_m are concerned, a similar tendency can be observed; namely, an increase of the ΔH_m value with the number of CH_2 groups takes

TABLE 1 Thermal Characteristics of the Investigated Perfluorooctyl Alkanes

Compound	T_m^a [on heating/ cooling] (°C)	T_{pt}^b [on heating/ cooling] (°C)	ΔH_m^c (kJ/mol)	ΔH_{pt}^d (kJ/mol)
F8H8	—/—	20.7/18.3	—	14.7
F8H9	—/—	33.3/29.1	—	24.4
F8H10	15.3/—	33.0/28.8	3.0*	16.1
F8H11	37.4/27.9	—/32.7	12.1	19.6
F8H12	32.7/26.7	—/—	22.6	—
F8H13	43.4/37.8	—/—	27.1	—
F8H14	43.4/39.6	—/—	26.1	—
F8H15	49.7/46.6	—/—	33.4	—
F8H16	53.1/48.2	—/—	39.1	—

[a] T_m, transition temp. (cryst. ⟷ isotropic or smectic).

[b] T_{pt}, transition temp. (smectic ⟷ isotropic).

[c] ΔH_m, transition enthalpy corresponding to T_m.

[d] ΔH_{pt}, transition enthalpy corresponding to T_{pt}.

*substance may contain certain amounts of "supercooled smectic phase" at temperatures less than 15°C.

place. The ΔH_{pf} values were calculated for the perfluorooctyl-n-alkanes with shorter hydrogenated moiety. The value of ΔH_m for F8H10 is small (ca. 3 kJ/mol) in comparison with its ΔH_{pt} (ca. 16 kJ/mol), whereas in the case of F8H11, the situation is quite different and the ΔH_{pt} and ΔH_m are comparable (19.6 and 12.1 kJ/mol, respectively).

Because of the characteristic phase transition, which can be noticed in DSC curves of F8H10 and F8H11, the detailed texture analysis was performed for those compounds. The textures of F8H10 are shown in Fig. 3. Upon cooling from the isotropic liquid, mosaic textures, characteristic for the smectic B phase, are visible (Fig. 3a). On further cooling, some cracks appeared, the number of which increased with lowering of the temperature. The number of cracks was found to be dependent on the rate of cooling (increasing upon the reduction of the cooling rate). Taking into consideration the DSC curves and the microscopic images in polarized light, the behavior of F8H10 can be interpreted as follows. The compound is liquid crystalline within the temperature range from ca. 15°C (phase transition observed in DSC curve) to ca. 33°C (clearing point). In microscopic measurements, we did not observe any sharp transition because the sample of F8H10 tends to supercool and form a metastable phase. At temperatures less than 15°C, the textures are still mosaic, indicating a smectic B phase, but the cracks appearing upon further cooling indicate recrystallization. This is clearly visible in Fig. 3, where the texture 3a, recorded at ca. 30°C, is mosaic; 3b is intermediate and cracked, whereas 3c seems to be a 3D crystal.

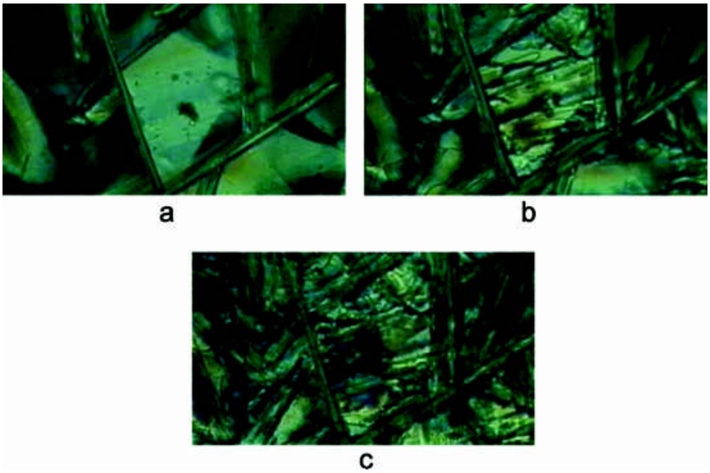

FIGURE 3 Textures of F8H10: a) T = 18.5°C, b) T = −13.2°C, c) T = −47.4°C.

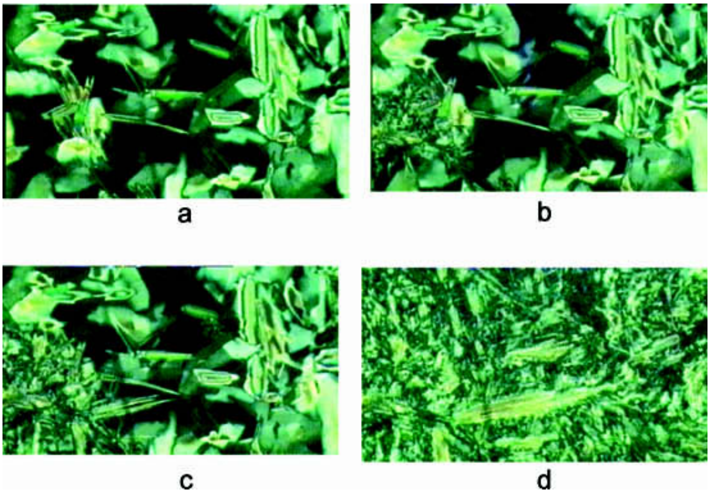

FIGURE 4 Textures of F8H11: a) T = 32.9°C, b) T = 28.8°C, c) T = 28.7°C, d) T = 28.3°C; heating rate: 0.2°min^{-1}.

The behavior of F8H11 differs from both F8H10 and all the remaining perfluorooctyl-n-alkanes investigated here. The microscopic images of this compound are presented in Fig. 4. On cooling, the mosaic texture, indicating a smectic B phase, was observed (Fig. 4a), but upon further cooling at ca. 28°C a quick recrystallization occurred, which is registered in Fig. 4b,c. Figure 4d shows a texture characteristic of a 3D crystal. The results are in accordance with the calorimetric measurements, indicating a crystal ⟷ smectic transition at ca. 28°C. Similar results were described for F10H11 and F10H12 [17].

As far as the perfluorooctyl alkanes with a longer hydrogenated moiety ($n > 11$) are concerned, liquid-crystalline textures were not observed, which is in agreement with the results published previously for perfluorodecyl-n-alkanes [17]. Regarding perfluorooctyl-n-alkanes with short hydrogenated fragment ($n < 10$), the textures were mosaic, characteristic of the smectic B phase, regardless of the rate of cooling/heating, and could be observed within a broad temperature range. No peaks indicating smectic ⟷ crystalline phase transition are present in the DSC curves registered for these compounds. This can suggest that the compounds are smectic at room temperature, their transition into 3D phase is of low energy, and they exhibit a pronounced tendency to supercool and form a metastable phase, which is supported by the fact that, even at low temperature and low rate of cooling, no recrystallization of the F8H8 and F8H9 samples was observed.

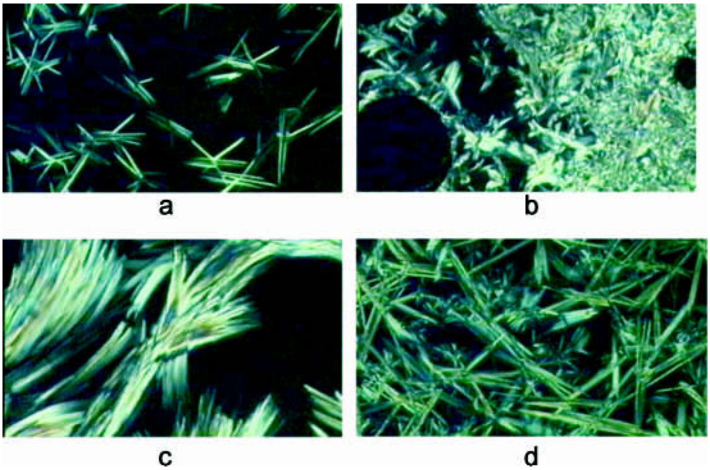

FIGURE 5 Textures of perfluoroisononyl-n-alkanes: a) iF9H7 (T= –17.3°C), b) iF9H10 (T=13.3°C), c) iF9H11 (T=27.9°C), d) iF9H15 (T=39.1°C).

Microscopic measurements in polarized light were carried out for all the investigated perfluoroisononyl-n-alkanes, and the results for selected representatives are presented in Fig. 5. Generally, the observed textures are typical for 3D crystals, regardless of the length of the hydrogenated fragment and the experimental conditions. It is interesting that a minute branching of the perfluorononyl chain changes the properties of perfluoroisononyl-n-alkanes so dramatically *versus* perfluorooctyl-n-alkanes as far as their crystalline/liquid-crystalline properties are concerned.

Calorimetric measurements were conducted for all the investigated perfluoroisononyl-n-alkanes, and the resultant DSC curves are separated into three groups: iF9H7, iF9H8, and iF9H10 (Fig. 6a), iF9H9, iF9H11, and iF9H12 (Fig. 6b); and perfluoroisononyl-n-alkanes with $n > 12$ (Fig. 6c). The DSC curves of the investigated perfluoroisononyl-n-alkanes are similar—only one peak, indicating melting of the sample (crystal $\longleftrightarrow$ isotropic transition), is present, and no additional peaks, characteristic for phase transitions, can be noticed. From the DSC curves, melting enthalpies have been calculated and together with the melting and freezing temperatures are compiled in Table 2. An odd–even effect is noticeable, especially for shorter homologues; for example, the melting temperature of iF9H9 is 23°C, whereas iF9H10 melts at ca. 16°C. Similar to perfluorooctyl-n-alkanes, for the series of perfluoroisononyl-n-alkanes, freezing temperatures are 4 to 6°C lower than the corresponding melting points.

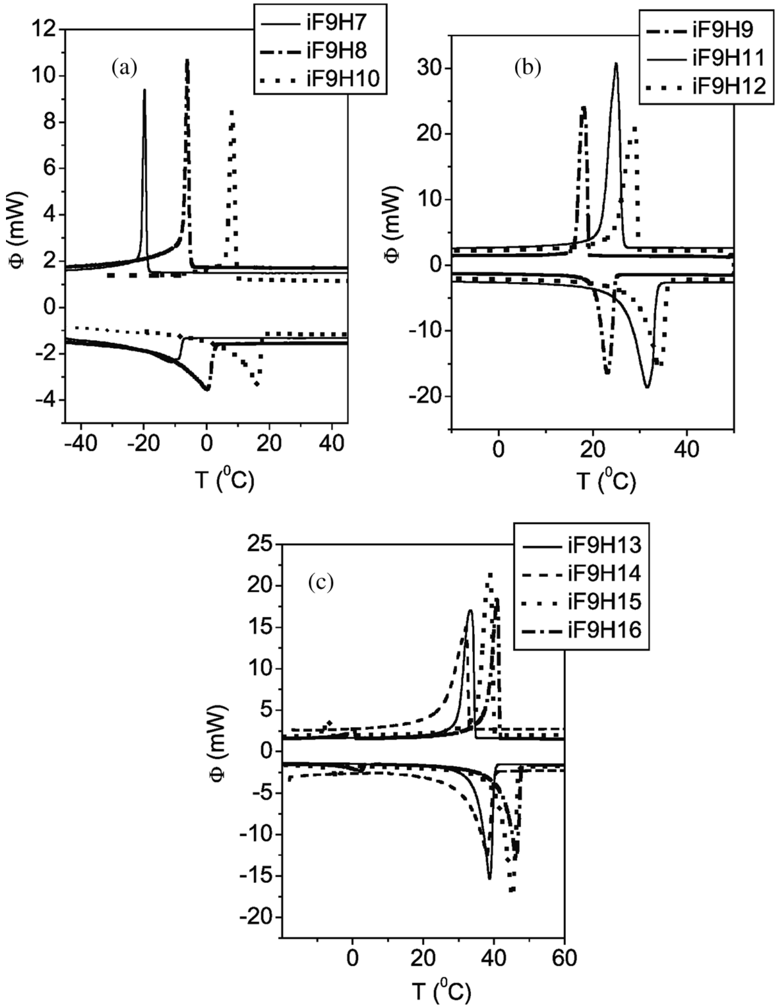

FIGURE 6 DSC curves for the investigated perfluoroisononyl-n-alkanes.

4. DISCUSSION

Perfluorooctyl-n-alkanes form similar liquid-crystalline phases to those described previously for perfluorodecyl-n-alkanes [17]. Similar phase transitions were observed for F8H11 and F10H11; however, F8H12 does not exhibit liquid-crystalline properties, in contrast to F10H12. Short perfluorooctyl-n-alkanes (n = 8, 9) are smectic at room temperature, and no recrystallization is seen on cooling. For F8H10

TABLE 2 Thermal Characteristics of the Investigated Perfluoroisononyl Alkanes

Compound	T_m^a [on heating/cooling] (°C)	ΔH_m^b (kJ/mol)
iF9H7	–11.2/–19.9	9.1
iF9H8	–0.7/–6.1	12.7
iF9H9	23.1/18.0	32.1
iF9H10	16.4/8.2	14.8
iF9H11	32.0/24.8	29.8
iF9H12	35.1/28.6	32.2
iF9H13	35.4/32.9	38.5
iF9H14	39.4/32.0	30.4
iF9H15	45.9/38.7	38.5
iF9H16	46.5/40.7	40.4

[a] T_m, transition temperature (crystalline ⟷ isotropic).
[b] ΔH_m, transition enthalpy corresponding to T_m.

and F8H11, characteristic phase transitions were observed. Perfluorooctyl-n-alkanes of longer hydrogenated fragment ($n > 11$) are not capable of liquid-crystalline phase formation. In contrast to perfluorooctyl-n-alkanes, perfluoroisononyl-n-alkanes do not form liquid, crystalline phases, regardless the length of the polymethylene chain and the experimental conditions applied. It is very interesting that a minute branching of the perfluorinated moiety profoundly affects the properties of SFA in the solid state. From literature it is known that some derivatives of SFAs possessing a halogen atom attached to the hydrogenated part either in the middle of SFA molecule [16] or at the terminal position [18] exhibit liquid-crystalline phases. However, no studies have been performed so far for SFAs containing a substituent or branching in the perfluorinated fragment. From our results, it can be concluded that the presence of CF_3 branching in the terminal position of the perfluorinated moiety results in higher molecular ordering. This, in fact, can be expected taking into consideration that for classic mesogens branching in the polymethylene chain leads to the loss of liquid-crystalline properties and, simultaneously, to higher ordering of molecules [12]. It would be of utmost importance to further the investigations and perform X-ray experiments to get deeper insight into the difference in molecular packing of normal *versus* iso chains.

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REFERENCES

[1] Scott, R. L. (1948). *J. Am. Chem. Soc.*, *70*, 4090.

[2] Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Cornell University Press: Ithaca, NY.

[3] Bunn, C. W. & Howells, E. R. (1954). *Nature*, *174*, 549.

[4] Brace, N. O. (1962). *J. Org. Chem.*, *27*, 3033.

[5] Rabolt, J. F., Russell, T. P., & Twieg, R. J. (1984). *Macromolecules*, *17*, 2786.

[6] Turberg, M. P. & Brady, J. E. (1988). *J. Am. Chem. Soc.*, *110*, 7797.

[7] Binks, B. P., Fletcher, P. D. I., Sager, W. F. C., & Thompson, R. L. (1995). *Langmuir*, *11*, 977.

[8] Binks, B. P., Fletcher, P. D. I., & Thompson, R. L. (1996). *Ber. Bunsenges. Phys. Chem.*, *100*, 232.

[9] Höpken, J., Pugh, C., Richtering, W., & Möller, M. (1988). *Makromol. Chem.*, *189*, 911.

[10] Gaines, G. L. Jr. (1991). *Langmuir*, *7*, 3054.

[11] Mahler, W., Guillon, D., & Skoulios, A. (1985). *Mol. Cryst. Liq. Cryst. Lett.*, *2*(3–4), 111.

[12] Stegemeyer, H. (1994). *Liquid Crystals*, Steinkopff Darmstadt, Springer: New York.

[13] Kirsch, P. (2004). *Modern Fluoroorganic Chemistry*, Wiley-VCH Verlag: Weinheim.

[14] Viney, C., Russell, T. P., Depero, L. E., & Twieg, R. J. (1989). *Mol. Cryst. Liq. Cryst.*, *168*, 63.

[15] Viney, C., Twieg, R. J., Russell, T. P., & Depero, L. E. (1989). *Liq. Cryst.*, *5*, 1783.

[16] Viney, C., Twieg, R. J., & Russell, T. P. (1990). *Mol. Cryst. Liq. Cryst.*, *182B*, 291.

[17] Broniatowski, M., Dynarowicz-Łątka, P., & Witko, W. (2005). *J. Fluorine. Chem.*, *126*, 79.

[18] Wang, J. & Ober, C. K. (1999). *Liq. Cryst.*, *26*, 637.