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Liquid crystal and gel properties of fluorine containing compound

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ABSTRACT

A series of (2-perfluorohexyl)-ethoxy phenyl 4-alkyl benzoate (F_6H_2OPCnB) was synthesized, and liquid crystals (LCs) and gelation properties were studied. The isotropic temperature (T_1) showed good even-odd effect. The compound with an odd number of carbon atoms in the alkyl chain possessed a higher temperature. T_m showed weak even-odd effect. However the transition showed an opposite alternation. The mesomorphic structure of those compounds was smectic A or E. The structure of the compound was bimolecular kinked structure. F_6H_2OPCnB gel (10 wt.% in propylene carbonate) was studied. T_{gel} of $F_6H_2OPC_2B$ showed the highest value due to its high T_m (crystal melting temperature). T_{gel} (gel melting temperature) was strongly dependent on T_m . $F_6H_2OPC_6B$ gel showed the highest value in heat of fusion. The gel's heat of fusion was a good parameter of the gel stability.

KEYWORDS

DSC; fluorocarbon; gelation; microscopic texture; smectic A and E; XRD

Introduction

Fluorocarbons and hydrocarbons possess different properties and are incompatible with one another. Those are due to the different chemical structure of H and F atoms leading to different chain conformations; $(CH_2)_n$ segments arrange in the usual zigzag conformation with a cross-sectional area of 18.5 Å² molecule, whereas a $(CF_2)_m$ chain possesses a typical 15/7 helix conformation and cross-sectional area of 28 Å²/molecule [1, 2]. When fluorocarbons are substituted for alkanes in calamitic liquid crystals (LCs), both the transition temperature and the temperature range of mesophase stability are increased. This is due to the increased rigidity of the fluorocarbon moities, which enhances the linearity of molecules relative to their alkane counterparts [3]. However, the intrinsic incompatibility between the fluorocarbon tails and the hydrocarbon mesogenic core leads to a nanophase separation of the chemically distinct components which results in layered (smectic) structure composed of fluorocarbon-rich and hydrocarbon-rich strata [3–6].

In our earlier paper, we described liquid crystalline properties of 4-(2-perfluorohexyl)ethoxy- cyanobiphenyl (F_6H_2OCB) and (2-perfluorooctyl)-ethoxy phenyl 4-methoxy benzoate(F_8H_2OPMB) which showed smectic K phase, and such a stable smectic K LC was rarely reported [7–8].

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Figure 1. The structure of F_6H_2 OPCnB.

We are interested in liquid crystal and gelation properties of a new homologous series of (2-perfluorohexyl)-ethoxy phenyl 4-alkyl benzoate(F_6H_2OPCnB), where n indicate the carbon numbers of the alkyl chain. The chemical structure was shown in Figure 1.

In this paper, we present LC and gelation properties of a series of F_6H_2OPCnB , and the results will be discussed in terms of the structure of the molecules.

Experimental

(2-perfluorohexyl)-ethoxy-4-methoxybenzene (F₆H₂OMB)

IH, IH, 2H, 2H-perfluoro-1-octanol (3.64g, 10 mmol), 4-methoxyphenol(1.24g, 10 mmol) and triphenylphosphine (2.62g, 10 mmol) were dissolved in dry tetrahydrofuran (THF) (30ml). Diisopropyl azodicarboxylate (2cc, 10 mmol) was added dropwise to the solution for 30 minutes under N₂ at 0°C. The solution was stirred at 0°C overnight under N₂ atmosphere. After quenching with cold water (1 ml), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent 2.5:1 hexane and ethyl acetate), and recrystallized in 95% ethanol to produce (2-perfluorohexyl)- ethoxy-4-methoxybenzene (F₆H₂OMB) as a white crystal (0.25g) in 5% yield. ¹H NMR confirmed the structure as (δ (ppm)) 6.78 (singlet, 4H), 4.25 (triplet, 2H), 3.80 (singlet, 3H), 2.62 (multiplet, 2H).

(2-perfluorohexyl)-ethoxy-4-hydroxybenzene

(2-Perfluorohexyl)-ethoxy-4-methoxybenzene (11.2 g, 22 mmol) was dissolved in dichloromethane (50 ml). Boron tribromide (5.1 cc, 53 mmol) in dichloromethane (50 ml) was added dropwise to the solution at 0°C. The solution was stirred at room temperature overnight. After quenching with cold water (5 ml), the solvent was removed under reduced pressure. The residue was dissolved by the addition of 100 ml of ether. The organic layer was separated and extracted with water, 10% NaHCO₃ and water. The ether extract was dried over anhydrous magnesium sulfate and recrystallized in toluene to produce (2-perfluorohexyl)-ethoxy-4-hydroxybenzene as a white crystal (10.6 g) in 87% yield. ¹H NMR confirmed the structure as (δ (ppm)) 6.83 (doublet, 2H), 6.79 (doublet, 2H), 4.78 (singlet, 1H), 4.24 (triplet, 2H), 2.62 (multiplet, 2H).

(I2-perfluorohexyl)ethoxyphenyl-4-alkylbenzoate (F₆H₂OPCnB)

(2-Perfluorohexyl)-ethoxy-4-hydroxybenzene (0.49 g, 1 mmol), 4-alkylbenzoyl chloride (1 mmol) and pyridine (0.16 cc, 2 mmol) were dissolved in chloroform (25 ml). The solution was stirred for 3 hours at room temperature. After quenching with cold water (1 ml), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent 2.5:1 hexane and ethyl acetate), and recrystallized in 95% ethanol to produce (2-perfluorohexyl)-ethoxyphenyl-4-alkylbenzoate (F_6H_2OPCnB) as a white crystal in 58% yield. ¹H NMR confirmed the structure as (δ (ppm)),

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- for n = l, 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.6 (multiplet, 2H), 2.45 (triplet, 3H),
- for n = 2, 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (quartet, 2H), 2.6 (multiplet, 2H), 1.2 (triplet, 3H),
- for n = 4, 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (multiplet, 2H), 2.6 (multiplet, 2H), 1.6 (multiplet, 2H) 1.35 (multiplet, 2H), 0.95 (triplet, 3H),
- for n = 5, 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (multiplet, 2H), 2.6 (multiplet, 2H), 1.65 (multiplet, 2H) 1.35 (multiplet, 4H), 0.9 (triplet, 3H),
- for n = 6, 8.07 (doublet, 2H), 7.30 (doublet, 2 H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (multiplet, 2H), 2.6 (multiplet, 2H), 1.65 (multiplet, 2H) 1.35 (multiplet, 6H), 0.9 (triplet, 3H),
- for n = 7, 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (multiplet, 2H), 2.6 (multiplet, 2H), 1.65 (multiplet, 2H) 1.32 (multiplet, 8H), 0.9 (triplet, 3H),
- for n = 8, 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (multiplet, 2H), 2.6 (multiplet, 2H), 1.65 (multiplet, 2H) 1.30 (multiplet, 10H), 0.9 (triplet, 3H),
- for n = 10, 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (multiplet, 2H), 2.6 (multiplet, 2H), 1.65 (multiplet, 2H) 1.30 (multiplet, 14H), 0.9 (triplet, 3H).

(2-perfluorohexyl)-ethoxyphenyl-4-propylbenzoate (F₆H₂OPC₃B)

4-(Dimethylamino)pyridine(DMAP) (0.08 g, 0.7 mmol) was added to a solution of 1-(2perfluorohexyl)-ethoxy-4-hydroxybenzene (0.49 g, 1 mmol), 4-propyl benzoic acid (0.16 g, 1 mmol) and N,N'-dicyclohexylcarbodiimide(DCC) (0.28 g, 1.4 mmol) in dichloromethane (25 ml). The solution was stirred for 26 hours at room temperature. After quenching with cold water (1 ml), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent 2.5:1 hexane and ethyl acetate), and recrystallized in 95% ethanol to produce (2-perfluorohexyl)-ethoxyphenyl-4-propylbenzoate (F₆H₂OPC₃B) as a white crystal (0.40 g) in 60% yield. ¹H NMR confirmed the structure as (δ (ppm)) 8.07 (doublet, 2H), 7.30 (doublet, 2H), 7.15 (doublet, 2H), 6.95 (doublet, 2H), 4.31 (triplet, 2H), 2.67 (multiplet, 2H), 2.6 (multiplet, 2H), 1.7 (multiplet, 2H), 1.0 (triplet, 3H).

Differential scanning calorimetry (DSC) was performed on a TA DSC Q20 (TA Instruments, New Castle, DE, USA) with ~ 10 mg sample using a scanning rate of 10° C min⁻¹ •.

Optical microscope evaluation was carried out using Olympus BX41 (Olympus Co., Shinjuku, Tokyo, Japan) polarizing microscope equipped with a Mettler FP82HT (Mettler Toledo AG, Im Langacher, Greifensee, Switzerland) hot stage.

The XRD data was collected between 5° and 60° 2 θ with a step increment of 0.02° 2 θ and a count time of 2 s/step. The well-known Bragg's equation ($\lambda = 2d \sin\theta$) was used to calculate the *d* spacing, wherein λ is a wavelength of 0.154 nm, *d* is the distance between each adjacent crystal plane (*d* spacing), and θ is the Bragg angle.

Gel test was processed as follows. 1 part of sample was mixed with 9 parts propylene carbonate in a liquid DSC cell and sealed the cell. The mixture was heated to 150° C until the solid was well dissolved. The resulting solution was cooled at room temperature for 1 hour, then the T_{gel} and the heat of fusion was checked by DSC.



n = 1 ~ 10

Figure 2. Synthesis of F₆H₂OPCnB.

Results and discussion

Synthesis

 F_6H_2OMB was synthesized by Mitsunobu reaction as shown in Figure 2. Boron tribromide was used for demethylation of methoxyphenyl, and fortunately 2-perfluorohexyl-ethoxy group was stable in this condition. Esterification was carried by conventional method, and the reaction scheme was shown in Figure 2.

Mesomorphic Properties

Liquid crystalline transition temperatures of F_6H_2 OPCnB in bulk state measured by DSC (Figure 3) were summarized in Table 1 and were plotted against hydrocarbon chain length, n, in Figure 4. The T_1 showed even-odd effect, The T_1 of the compounds with an odd number of carbon atoms in the alkyl chain possessed a higher curve compared to those with even

n	T _m (°C)	$\Delta H(J/g)$	T ₁ (°C)	$\Delta H(J/g)$
1	85.91	60.23	133.59	10.09
2	103.19	39.46	125.93	7.76
3	72.31	31.59	131.39	9.06
4	73.84	42.29	125.62	9.78
5	69.47	38.38	127.84	10.30
6	69.96	37.45	122.29	11.38
7	68.67	35.27	123.31	12.79
8	72.03	39.90	115.93	11.76
10	72.17	35.46	110.02	12.82

Table 1. The liquid crystalline transition temperature of F_6H_2 OPCnB.





number of atoms in their alkyl chains. This alternation of T_I between odd and even numbers of the series was most pronounced for short length alkyl chain. Extension of the hydrocarbon chain length caused decrease of the melting point. The T_m also showed weak even odd effect. However the T_m showed an opposite alternation. Extension of the hydrocarbon chain length also causes decreased of T_m and reached a minimum value at n = 7. The liquid crystallinity of compound with an odd number of carbon atoms in the alkyl chain showed higher stability, wide LC temperature range and high isotropic temperature. The compound, $F_6H_2OPC_2B$ (n = 2), showed dramatic decrease of LC temperature range and high melting temperature. This result also should be explained.



Figure 4. The plot of liquid crystalline transition temperature vs n of F₆H₂OPCnB.



Figure 5. Fan-shaped texture of F₆H₂OPC₁B at 111°C (200x).

The latent heat of the crystal to smectic transition (31.6-60.23 J/g) was larger than that of smectic to isotropic transition (7.8-12.8 J/g). The smectic phase was assumed to have lower order molecular arrangement like smectic A phase. Mesomorphic microscopic texture of the compounds in Figure 5 showed fan shape texture characteristic of smectic A and E.

X-ray diffraction method was used for studying the structure and property relationship. X-ray diffraction pattern and calculated d_{100} were in table 2 and Figure 6 and 7. The structure of

n	d ₁₀₀ (A)	d ₂₀₀	d ₃₀₀	d ₄₀₀
1	34.84	17.43		8.65
2	33.84		11.03	
3	35.12		11.71	
4	37.77	18.64	12.57	
5	38.60		12.84	
6	38.82		12.94	
7	39.13	19.56		
10	40.23			10.06

Table 2.	The d_{10}	vsno	of F _e H	OPCnE
10010 21		,	21 1 611	,01 0110



Figure 6. X-ray diffraction patterns of F_6H_2 OPCnB.

the compounds was proposed as a bimolecular structure due to the volume difference of the two parts (fluorocarbon and hydrocarbon). The measured interlayer distance (*d*) was slightly less than the calculated dimer molecular length (L), The difference could be explained by Kink model [7], The kink angle (θ) of fluorocarbon was calculated by comparison of *d* (34.84 A) and L(36.84 A), calculated value was $\theta = 23^{\circ}$ for F₆H₂OPC₁B. The *d* of the compound, F₆H₂OPC₂B (n = 2), was less than that of F₆H₂OPC₁B (n = 1), which could be explained by higher kink angle. The big kink angle reduced the molecular length and increase density, which caused higher melting point. The molecular length difference along the carbon atoms in the alkyl chain was about 0.6 A ((40.23–34.84)/9 = 0.6), which was less than 1.3 A for that of extended structure. So the conformation of the alkyl chain in the tail was a random coil



Figure 7. The plot of d $_{100}$ vs n of F_6H_2 OPCnB.

conformation. The characteristic peaks of smectic E in X-ray were strong in intensity at 002 and 003 reflections. The type of liquid crystal might be smectic E for the compounds (n = 2,3,5,6 of F_6H_2OPCnB). Sidechain crystallization peaks were also shown at 4.61 and 4.51 for n = 8, at 4.67 and 4.52 for n = 10 of F_6H_2OPCnB .

Gel properties

The phase transition behavior of the gel samples was examined by DSC. The DSC thermogram and data of the gel samples were shown in Table 3 and Figure 8 and 9. The T_{gel} increased proportional to the gelator concentration at lower region and became a plateau at ca. 10 wt.% gelator concentration [9). So the concentration of all the gel was fixed at 10 wt.% in propylene carbonate. The consideration criteria of gel stability were [10], (1) the sol to gel transition temperature (T_{gel}) (2) the critical gel concentration (cgc) (3) the heat of fusion of the gels etc. T_{gel} was changed greatly with n, and there were no trends with the number of carbon in the alkyl chain. But with careful examination of the data, we found that T_{gel} is similar to T_m . Thus T_{gel} was greatly dependent on T_m . T_{gel} of $F_6H_2OPC_2B$ showed the highest value due to its high T_m . But it was difficult to say whether the gel had the highest gel stability.

n	T _{gel} (C)	ΔH (J/g)
1	88.21	3.098
2	104.62	3.121
3	60.19	1.079
4	70.31	1.320
5	71.56	4.231
6	72.77	4.611
7	70.69	2.884
8	71.35	1.959
10	72.27	1.875

Table 3. The T_{ael} and heat of fusion of the gel vs *n* of F_6H_2OPCnB solution in 10 wt.% propylene carbonate.



Figure 8. DSC thermograms of F_6H_2 OPCnB gel in 10 wt.% propylene carbonate.

Heat of fusion of the gel was a good parameter of gel stability. Heat of fusion value in n = 1 and 2 of F_6H_2OPCnB was medium, that of n = 3 and 4 was low, and that of n = 5 and 6 was high. For n > 6, heat of fusion of the gel decreased with increasing n. Thus, coupling of biphenyl ring in the gel showed strong intermolecular interaction. And the length of alkyl group in the tail having the same length of fluorocarbon showed highest stability.



Figure 9. The plot of T_{qel} and heat of fusion of the gel vs n of F_6H_2 OPCnB gel in 10 wt.% propylene carbonate.

Conclusion

A series of F_6H_2 OPCnB exhibited fan shape texture characteristic of smectic A and E. The isotropic temperature showed good even-odd effect. The compound with an odd number of carbon atoms in the alkyl chain possessed a high temperature. T_m showed weak even-odd effect. However the transition showed an opposite alternation. The structure of the compound proved by X-ray diffraction was bimolecular kinked structure. Kink angle of F_6H_2 OPC₁B was 23°. F_6H_2 OPCnB gel (10 wt.% in propylene carbonate) was also studied. T_{gel} was greatly dependent on T_m . Heat of fusion of the gel was a good parameter of the gel stability. Heat of fusion of F_6H_2 OPC₆B had the highest value.

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