Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Gelation of 1-Alkoxy-4-(2-Perfluoroalkyl)Ethoxybenzenes in Organic Solvents

Yuki Morita [a], Takeyasu Tasaka [a], Kosuke Kawabe [a], Hiroaki Okamoto [a], Shunsuke Takenaka [a] & Hidetoshi Kita [a]

[a] Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi, Japan

Version of record first published: 31 Aug 2006

To cite this article: Yuki Morita, Takeyasu Tasaka, Kosuke Kawabe, Hiroaki Okamoto, Shunsuke Takenaka & Hidetoshi Kita (2005): Gelation of 1-Alkoxy-4-(2-Perfluoroalkyl)Ethoxybenzenes in Organic Solvents, Molecular Crystals and Liquid Crystals, 435:1, 153/[813]-162/[822]

To link to this article: http://dx.doi.org/10.1080/15421400590957107

Mol. Cryst. Liq. Cryst., Vol. 435, pp. 153/[813]–162/[822], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590957107

Taylor & Francis
Taylor & Francis Group

Gelation of 1-Alkoxy-4-(2-Perfluoroalkyl)Ethoxybenzenes in Organic Solvents

Yuki Morita
Takeyasu Tasaka
Kosuke Kawabe
Hiroaki Okamoto
Shunsuke Takenaka
Hidetoshi Kita
Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube Yamaguchi, Japan

This paper describes preparation and physico-chemical properties of 1-alkoxy-4-(2-perfluoroalkyl)ethoxybenzenes (FmOOCn). For FmOOCn, 4-F(CF$_2$)$_m$CH$_2$CH$_2$O-phenyl-O-(CH$_2$)$_n$H, three homologues, m = 8 (n = 1, 2) and m = 10 (n = 1) reveal monotropic smectic A and unidentified smectic phases, respectively. Simultaneously, most of the homologous are possible to gelatinize various organic solvents such as octane, cyclohexane, DMF, ethanol, and so on. The gelation ability increases with increasing the carbon number of the perfluoroalkyl chain. The formed gel is transparent, semitransparent or opaque, and the phase transition between the gel phase and the isotropic fluid is thermally reversible. The images of gel observed with scanning electron microscope (SEM) show gathered fibrous aggregates.

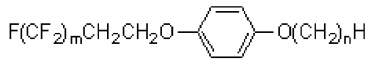
Keywords: fibrous aggregate; gelation; perfluoroalkyl chain; SEM; smectic phase

INTRODUCTION

Diblock semifluorinated *n*-alkanes were studied in recent years in relation to their interesting peculiarities such as excellent liquid crystallinity and gel formation ability in organic solvents [1–4]. In our earlier paper, we described liquid crystal properties of alkyl

This work was partially supported by the Mazda Foundation.

Address correspondence to Yuki Morita, Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2557, Ube, Yamaguchi 755-8611, Japan. E-mail: y-morita@po.cc.yamaguchi-u.ac.jp



F*m*OOC*n*

FIGURE 1 Structure of F*m*OOC*n*.

4-(2-perfluoroalkyl)ethoxybenzoates, and clarified that 2-(perfluoroalkyl)ethoxybenzene is an excellent segment for liquid crystal materials as compared with the other substituted benzenes such as perfluoroalkylbenzenes, perfluoroalkylmethoxybenzenes, and so on, though preparation is not so easy [5,6]. In this connection, we are interested in the liquid crystal and gelation properties of a new homologous series of 1-alkoxy-4-(2-perfluoroalkyl)ethoxybenzenes, F*m*OOC*n*, where *m* and *n* indicate the carbon numbers of the perfluoroalkyl and alkoxy chains, respectively.

The chemical structure is shown in Figure 1.

In this paper, we present liquid crystal (LC) and gelation properties of F*m*OOC*n*, and the results will be discussed in terms of physical properties of the molecules.

EXPERIMENTAL

Materials

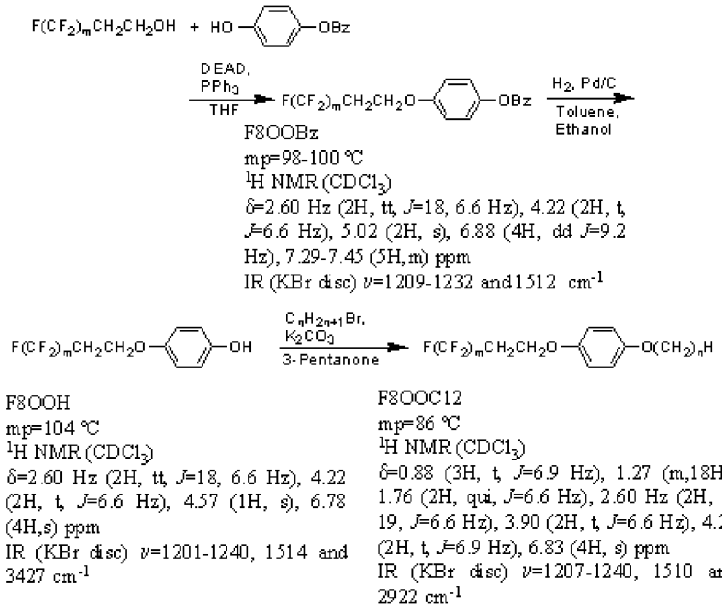
F*m*OOC*n* were prepared according to Scheme 1.

1-Benzyloxy-4-(2-perfluorooctyl)ethoxybenzene

2-Perfluorooctylethanol (23.2 g, 50 mmol), 4-benzyloxyphenol (10.0 g, 50 mmol) and triphenylphosphine (13.1 g, 50 mmol) were dissolved in dry THF (150 mL), and DEAD (8 mL, 51 mmol) was added dropwise during 15 min under N_2 at 0°C. After stirring at 0°C for overnight, the mixture was quenched with cold water (1 mL). Then, the solvent was removed *in vacuo*. The residues were dissolved in ethanol, and the solution was cooled. White precipitates were collected by filtration and was purified by column chromatography on silica-gel (eluent $CHCl_3$) to give 1-benzyloxy-4-(2-perfluorooctyl)ethoxybenzene as colorless needles, 1.5 g (4.5%).

4-(2-Perfluorooctyl)ethoxyphenol

A suspension of 1-benzyloxy-4-(2-perfluorooctyl)ethoxybenzene (2.5 g, 3.9 mmol) and 5% Pd on charcoal (0.32 g) in a mixture of ethanol (100 mL) and toluene (100 mL) was stirred at room temperature for a



SCHEME 1 Synthesis of F*m*OOC*n*.

week under an atmosphere of H_2. After the catalyst was filtered off, the solvent was removed *in vacuo*. The residues were recrystallized from toluene to give 4-(2-perfluorooctyl)ethoxyphenol as colorless crystals, 1.2 g (56%).

4-(2-Perfluorooctyl)ethoxy-dodecyloxybenzene (F8OOC12)

4-(2-Perfluorooctyl)ethoxyphenol (0.25 g, 0.45 mmol), anhydrous potassium carbonate (0.08 g, 0.58 mmol) and 1-bromododecane (0.13 g, 0.52 mmol) were suspended in 10 mL of 3-pentanone, and the mixture was refluxed for 24 hours. After the precipitate was filtered off, the solvent was removed *in vacuo*, and the residues were purified by column chromatography on silica-gel (eluent $CHCl_3$) to give 4-(2-perfluorooctyl)ethoxy-dodecyloxybenzene (F8OOC12) as colorless powders, 0.16 g (50%).

The purity of each compound was checked by HPLC and ^{1}H NMR.

Method

Transition temperature and the mesomorphism in bulk state were characterized using a Nikon POH polarizing microscope fitted with a

Mettler thermo-control system (FP-900). A typical procedure for gelation test is as follows [7]: a weighed sample was mixed with an organic solvent in a sample tube with cap ($\phi 10 \times 34$ mm) and the mixture was heated until the solid was well dissolved. The resulting solution was cooled in a refrigerator and placed at room temperature for 1 hour. Then, the gelation was checked visually. When upon inversion of the sample tube there was no fluid running down the walls, and it was judged gel. When the samples caused gelation, the gelation ability was evaluated quantitatively by the critical gel concentration (cgc) which was the minimum concentrations of gelators necessary for gelation at room temperature. For preparation of SEM sample, F*m*OOC*n* was dissolved in ethanol or cyclohexane at the cgc in sample tube and a piece of thin glass was soaked in the solution. Then, the solvent was removed off by pumping *in vacuo* for 12 hours and the gel was loaded on a piece of thin glass. The SEM pictures were taken using Nihon-denshi JSM 6335 F NT.

RESULTS AND DISCUSSION

Transition temperatures for F*m*OOC*n* in bulk state are summarized in Table 1.

F8OOC1 and F8OOC2 exhibit smectic (Sm) phase having a common fan texture under a homogeneous alignment, however, the higher

TABLE 1 Transition Temperatures of F*m*OOC*n* in Bulk State

	Transition temperature/°C			
F*m*OOC*n*	C	Sm	Sm A	I
F8OOC1	. 60	-	(.52)	.
F8OOC2	. 67	-	(.58)	.
F8OOC3	. 60	-	-	.
F8OOC4	. 70	-	-	.
F8OOC5	. 72	-	-	.
F8OOC6	. 72	-	-	.
F8OOC8	. 78	-	-	.
F8OOC12	. 86	-	-	.
F8OOC14	. 87	-	-	.
F10OOC1	. 88	(.84)	-	.
F10OOC5	. 90	-	-	.
F10OOC8	. 96	-	-	.
F10OOC12	. 95	-	-	.

C, Sm, Sm A and I indicate crystal, unidentified smectic, smectic A and isotropic phases, respectively.

Parentheses indicate a monotropic transition temperature.

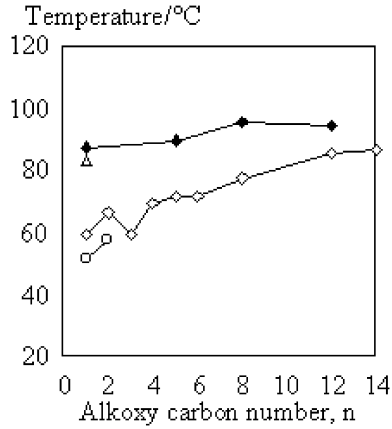


FIGURE 2 Plots of transition temperatures vs. n of F*m*OOC*n*. ◇: melting points of F8OOC*n*; ○: SmA-I (monotropic) transition temperatures of F8OOC*n;* ◆: melting points of F10OOC*n*; △: Sm-I (monotropic) transition temperature of F10OOC*n*.

members ($n > 2$) do not show any LC phase even in a cooling process. Therefore, it would be reasonable to assume that formation and thermal stability of the Sm phase are a subtle counterbalance between fluoro-and hydrocarbon chain lengths. The Sm phase was classified into the A (SmA) modification, since this phase is miscible with the SmA one of methyl and ethyl 4-(2-perfluorooctylethoxy)benzoates [5]. The transition temperatures are plotted against hydrocarbon chain length, n in Figure 2.

Extension of the hydrocarbon chain length causes a monotonous increase of melting point. These tendencies are also observed in LC properties of alkyl 4-(2-perfluoroalkyl)ethoxybenzoates [5]. F10OOC1 also exhibits a monotropic smectic (Sm) phase. The Sm phase has a fan texture and optically uniaxial nature. Considering the fact that latent heat of the Sm-I transition (18.9 kJ/mol) is larger than those of F8OOC1 (4.0 kJ/mol) and F8OOC2 (4.6 kJ/mol), the Sm phase is assumed to have higher ordered molecular arrangement than SmA phase. The higher homologs of F10OOC*n* ($n > 2$) do not exhibit any LC phase. These results also indicate that the subtle balance between fluoro- and hydrocarbon chain is important in exhibiting Sm phase.

Values of the cgc of F*m*OOC*n* are summarized in Table 2.

The gelation ability of F*m*OOC*n* increases with increasing the carbon numbers of both perfluoroalkyl and alkyl chains. F*m*OOC*n* can gelatinize various solvents, that is, alcohols such as methanol

TABLE 2 Values of the cgc (wt%) of F*m*OOC*n*

Solvent	F*m*OOC				
	F8OOC1	F8OOC5	F8OOC14	F10OOC1	F10OOC5
Methanol	5.3*	1.3 (op)	0.58 (op)	2.1 (op)	0.68 (op)
1-Octanol	8.0 (op)	1.3 (tr)	0.46 (tr)	1.5 (se)	0.39 (tr)
Octane	14 (tr)	4.8 (tr)	4.1 (op)	5.3 (tr)	2.7 (se)
Cyclohexane	11 (tr)	4.0 (tr)	4.1 (se)	3.3 (tr)	2.8 (tr)
Toluene	33 (se)	11 (se)	8.9 (se)	11 (op)	5.6 (se)
Acetonitrile	10 (op)	1.7 (se)	0.20(se)	3.8 (op)	0.26 (op)
N,N-dimethyl formamide	16 (tr)	1.6 (tr)	0.57 (tr)	1.8 (tr)	0.69 (tr)
Chloroform	23*	15*	11*	13*	7.5*

*Mixture of gel and crystal.
Abbreviation: op, opaque gel; tr, transparent gel; se, semitransparent gel.

and 1-octanol, hydrocarbons such as octane, cyclohexane, and toluene, and others such as chloroform, acetonitrile, *N*,*N*-dimethylformamide. The formed gel is transparent, semitransparent or opaque. The phase transition between the gel phase and isotropic fluid is thermally reversible, while the transition temperatures on the heating process are always higher than those on the cooling one. The effective order for gelation is given by:

$$\text{alcohols} > \text{polarsolvents} > \text{hydrocarbons} > \text{halogen solvents}.$$

It is considered that the criteria of gel stability are three points: (1) the critical gel concentration (cgc), (2) the sol-to-gel transition temperature (T_{gel}), (3) the duration of period that a gel persists in a sealed tube at room temperature without macroscopic phase separation or flowing when inverted [8].

Figure 3 shows the plot of the cgc of F8OOC*n* vs. the carbon number, n in 1-octanol.

The cgc of F8OOC*n* steeply decreases on ascending of n when $n < 5$, and becomes constant for the higher homologues ($n \geq 5$). For F8OOC1 and F8OOC2, crystallization and gelation simultaneously happen on the cooling process. For F8OOC3 and the higher members, formed gel is stable at room temperature for more than one week, without recrystallization.

The T_{gel} values of F8OOC*n* in 1-octanol are plotted vs. gelator concentration in Figure 4.

The T_{gel} increase in proportional to the gelator concentration at lower region and become plateau at ca. 10 wt% of gelator concentration. The

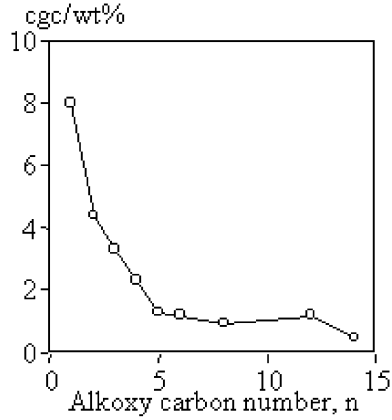


FIGURE 3 The cgc of F8OOC*n* vs. *n* in 1-octanol.

T_{gel}'s curves transfer upper with increasing n and their values become large with increasing n at the same gelator concentration.

In Figure 5 the T_{gel} values of F8OOC5 in various alcohols and octane is plotted vs. gelator concentration.

The lower the gelator concentration is at the onset of the plateau region, the higher the T_{gel} and the higher the gelation stability are. At the plateau region at higher gelator concentrations ($\geq$15 wt%) in alcohols except octane, the T_{gel} values are almost same. The order of gel stability is presented by: benzyl alcohol > 1-octanol > 1-butanol > ethanol > octane.

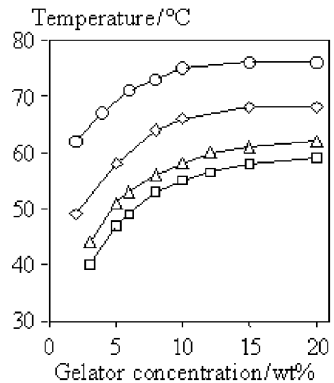


FIGURE 4 Sol-to-gel phase transition temperatures of F8OOC*n*, $n = 1$ (□), $n = 2$ (△), $n = 5$ (◇), and $n = 14$ (○) vs. gelator concentration in 1-octanol.

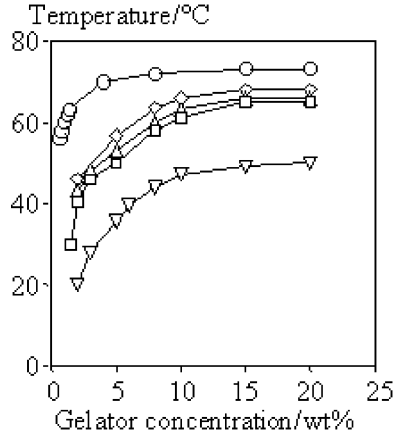


FIGURE 5 Sol-to-gel phase transition temperatures of F8OOC5 vs. gelator concentration in ethanol (□), 1-butanol (△), 1-octanol (◇), octane (▽), and benzyl alcohol (○).

It seems that some solubility of hydrocarbons as well as solvophobic force derived from perfluoroalkyl chains is one of the important factor to assemble in polar solvent.

The SEM photographs of gel for F8OOC5 formed in ethanol (a) and in cyclohexane (b) are shown in Figure 6.

The images in Figures 6(a) and (b) show many gathering fibrous aggregates, one of whose width is ca. ≥ 400 Å. Those aggregates form the three-dimensional network to immobilize the organic solvent, and finally cause physical gelation.

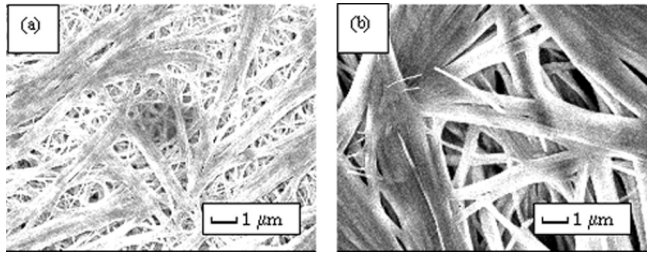


FIGURE 6 Scanning electron micrographs of F8OOC8 dispersed in organic solvents. (a) Gelator concentration: 1 wt% in ethanol and (b): Gelator concentration 3 wt% in cyclohexane, magnification ×10000.

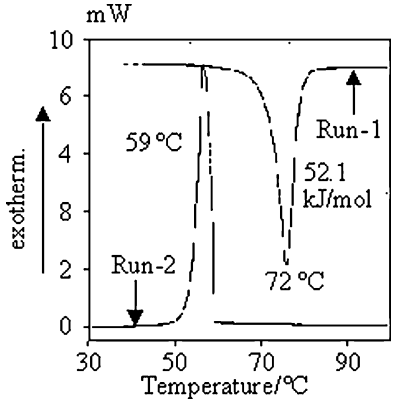


FIGURE 7 DSC thermograms of F8OOC5. Run-1: the first heating of the gel sample prepared for SEM observation. Run-2: the cooling of isotropic sample.

The phase transition behavior of the gel samples prepared for SEM observation was examined by differential scanning calorimeter (DSC), and the DSC thermograms of F8OOC5 are shown in Figure 7.

On the first heating process (Run-1) the gel sample shows an endothermic peak at 72°C (52.1 kJ/mol), which is comparable with those of solid formed from isotropic solution. On the cooling process (Run-2) an exothermic peak is observed at 59°C. The phase transition cycle is completely reversible. These results suggest that the gel state in Figure 6 is quite similar to the solid state in thermodynamic point of view.

CONCLUSIONS

For 1-alkoxy-4-(2-perfluoroalkyl)ethoxybenzenes (F*m*OOC*n*), F8OOC1 and F8OOC2 exhibit monotropic smectic A phase, and F10OOC1 exhibits a monotropic higher ordered Sm one. As the carbon number of alkoxy chains increases, F*m*OOC*n* ($n \geq 3$) do not show any mesophase. F*m*OOC*n* ($n \geq 3$) can gelatinize various organic solvents, which especially can gelatinize alcohols and other polar solvents at low concentrations ($0.5 \sim 2$ wt%). The formed gel is transparent, semitransparent or opaque, and the sol-to-gel phase transition is thermally reversible. The images of gathered fibrous aggregates are observed by SEM.

REFERENCES

[1] Twieg, R. J., Russell, T. P., Siemens R., & Rabolt, J. F. (1985). *Macromolecules*, *18*, 1361.
[2] Ishikawa, Y., Kuwahara, H., & Kunitake, T. (1994). *J. Am. Chem. Soc.*, *116*, 5579.

[3] Ku, C.-Y., Nostro, P. L., & Chen, S-H. (1997). *J. Phys. Chem. B.*, *101*, 908.
[4] Napoli, M., Conte, L., & Guerrato, A. (2001). *J. Fluorine Chem.*, *110*, 47.
[5] Duan, M., Okamoto, H., Petrov, V. F., & Takenaka, S. (1998). *Bull. Chem. Soc. Jpn.*, *71*, 2735.
[6] Duan, M., Okamoto, H., Petrov, V. F., & Takenaka, S. (1999). *Bull. Chem. Soc. Jpn.*, *72*, 1637.
[7] Hanabusa, K., Kobayashi, H., Suzuki, M., Kimura, M., & Shirai, H. (1998). *Colloid Polym. Sci.*, *276*, 252.
[8] Abdallah, D. J. & Weiss, R. G. (2000). *Langmuir*, *16*, 352.