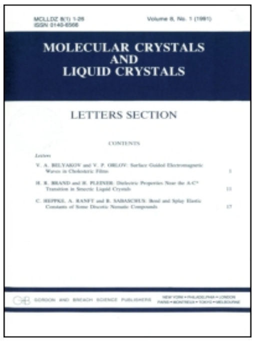


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis and physico-chemical properties of 2-alkoxy- 6-[4-(2-perfluorohexyl)ethylthiophenyl]naphthalene

Tomohiro Yoshida, Asami Ohashi, Yuki Morita & Hiroaki Okamoto

To cite this article: Tomohiro Yoshida, Asami Ohashi, Yuki Morita & Hiroaki Okamoto (2017) Synthesis and physico-chemical properties of 2-alkoxy- 6-[4-(2-perfluorohexyl)ethylthiophenyl]naphthalene, Molecular Crystals and Liquid Crystals, 647:1, 299-306, DOI: 10.1080/15421406.2017.1289617

To link to this article: http://dx.doi.org/10.1080/15421406.2017.1289617

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2017, VOL. 647, 299–306
http://dx.doi.org/10.1080/15421406.2017.1289617

Synthesis and physico-chemical properties of 2-alkoxy-6-[4-(2-perfluorohexyl)ethylthiophenyl]naphthalene

Tomohiro Yoshida[a], Asami Ohashi[a,b], Yuki Morita[a], and Hiroaki Okamoto[a]

[a]Graduate School of Science and Engineering, Yamaguchi University, Japan; [b]Asahi kasei E-materials Corporation, Japan

ABSTRACT
This paper describes the synthesis of and mesomorphic property and gelation ability for 2-Alkoxy- 6-[4-(2-perfluorohexyl)ethylthiophenyl] naphthalene (compounds **1**-n). Compounds **1**-n show exclusively a smectic A (SmA) phase, where the SmA–isotropic phase transition temperatures are 192°C for **1**-1 and 171°C for **1**-6. The SmA phase is characterized using a polarized microscope and DSC measurements. Interestingly, compounds **1**-n form physical gels (thermo-reversible gels) in *n*-octane, ethanol, and aprotic polar solvents such as acetonitrile and γ-butyrolactone, where the sol-gel transition temperatures are 60°C for **1**-1 and 80°C for **1**-6. The propylene carbonate gel is characterized by scanning electron microscope (SEM) observation, showing nano-fibers assembled with compound **1**-6.

KEYWORDS
Synthesis; Smectic A phase; Organic gelators; Organogels

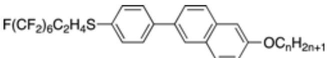
Introduction

Soft materials such as liquid crystal (LC) materials and molecular gels have attracted a great amount of great interest because they have much attention from theoretical and practical applications [1–4]. A lot of compounds have been investigated to determine the relationship between molecular structures and physical properties. Many LC materials have been reported now, where a rigid core and flexible terminal alkyl chain(s) are indispensable to exhibit a mesomorphic property. It has been known that perfluoroalkyl group tends to induce smectic properties probably due to fluorophilic and/or fluorophobic interactions [5–10].

Recently, many organic gelators have been also reported, and the researches are devoted to elucidate the relationship between the molecular structures and the gelation ability. The aggregation of organic gelators to fibrous network is driven by weak intermolecular interactions such as hydrogen bonding, dipole-dipole, van der Waals and π-π interactions [1–2]. In fact, many organic gelators reported are consist of two parts, that is, one is protic functional groups such as hydroxyl, amino, and carboxyl groups, and the other is aprotic ones, bulk aromatic core and/or long alkyl chains [11–12]. The introduction of perfluoroalkyl chain(s) is known as a common strategy to enhance the self-assembly such as gelation properties [1].

Several organic gelators having perfluoroalkyl chains were also prepared and it has been clarified that the perfluoroalkyl chain affects the gelation ability differently from the alkyl chains [13,14]. In our earlier papers, we have investigated that 4-(2-perfluorohexyl)butoxy

CONTACT Hiroaki Okamoto ✉ oka-moto@po.cc.yamaguchi-u.ac.jp
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.



Compounds **1**-n

Figure 1. Chemical structure for compounds **1**-n.

group affect their mesomorphic properties and gelation ability [15,16]. Furthermore, we have also reported some organic gelators having perfluoroalkyl chains at the both terminal positions of the molecule [17,18].

This paper describes synthesis, mesomorphic and gelation properties of perfluoroalkylated compounds with a 2-alkoxy-6-substituted naphthalene core (compounds **1**-n) as shown in Figure 1. The molecular structures are to incorporate neither protic function group nor so long hydrocarbon chain. The geometrical structure is simple, rod-like and very similar to the conventional LC materials.

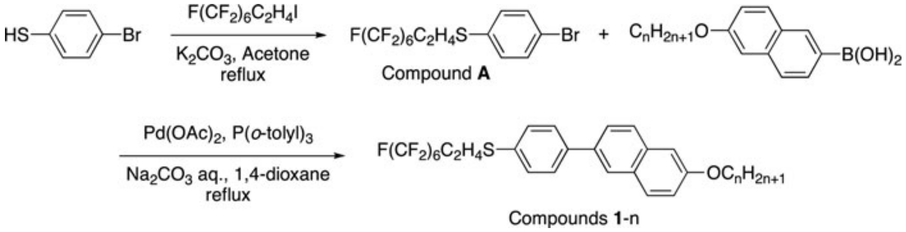
Experimental

Materials

Compounds **1**-n were synthesized according to Scheme 1, where compounds **1**-n and synthetic intermediates were characterized by means of IR and ^{1}H NMR spectra and high-resolution mass spectra (HRMS) were recorded with a Waters LCT Premier/XE^{TM}. The synthetic procedures are as follows.

4-[2-(Perfluorohexyl)ethylsulfanyl]bromobenzene (**A**): 2-(Perfluorohexyl)ethyl iodide (30.02 g, 63.33 mmol), 4-bromobenzenethiol (11.96 g, 63.29 mmol), and K_2CO_3 (13.29 g, 96.16 mmol) were added in acetone (100 mL) in a 300 mL recovery flask, and the resulting mixture refluxed for 1 day. The reaction mixture was allowed to cool to room temperature. Then saturated NaCl aqueous solution (100 mL) was added to the mixture, and the resulting solution was extracted with EtOAc (100 mL × 3). The organic layers were combined and dried with $MgSO_4$, and after filtration, the filtrate was concentrated using a rotary evaporator under reduced pressure. The crude product was purified by recrystallization (EtOH) to give 4-[2-(Perfluorohexyl)ethylsulfanyl]bromobenzene (**A**) (32.41g, 60.76 mmol) in 96% yield as colorless powder: mp = 43–44°C, IR (KBr disc): ν = 1248–1140 cm^{-1}, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.33–2.43 (2H, m), 3.09–3.12 (2H, m), 7.23 (2H, d, J = 8.5 Hz), 7.46 (2H, d, J = 8.5 Hz) ppm, HRMS (ESI): *m/z* calcd for $C_{14}H_7BrF_{13}S$ $[M - H]^-$ 532.9244; found 532.9285.

2-Methoxy-6-[4-(2-perfluorohexyl)ethylsulfanyl]phenyl]naphthalene (compound **1**-1): 4-[2-(Perfluorohexyl)ethylsulfanyl]bromobenzene (**A**) (13.38 g, 25.00 mmol), 6-methoxy-2-naphthylbronic acid (5.00 g, 24.75 mmol), Na_2CO_3 (5.30 g, 50.00 mmol), $Pd(OAc)_2$ (0.05 g, 0.9 mol%), and tri(*o*-tolyl)phosphine (0.15 g, 2 mol%) were added in 1,4-dioxane (40 mL)



Scheme 1. Synthetic scheme for compounds **1**-n.

and water (40 mL) in a 200 mL flask, and the mixture was refluxed for 12 h under N_2 atmosphere. The reaction mixture was allowed to cool to room temperature. Then saturated NaCl aqueous solution (100 mL) was added to the mixture, and the resulting solution was extracted with $CHCl_3$ (100 mL × 3). The organic phases were combined and dried with $MgSO_4$, and after filtration, the filtrate was concentrated using a rotary evaporator under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: $CHCl_3$) and recrystallization (EtOH: toluene = 8: 2) to give compound **1**-1 (14.55 g, 23.76 mmol) in 95% yield as colorless crystals.: IR (KBr disc): $\nu = 1236-1188\ cm^{-1}$, ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.40-2.50$ (2H, m), 3.12–3.15 (2H, m), 3.95 (3H, s), 7.17 (1H, d, 2.4 Hz), 7.18 (1H, dd, $J = 10.9$, 2.4 Hz), 7.47 (2H, d, $J = 8.5$ Hz), 7.68 (2H, d, $J = 8.5$ Hz), 7.69 (1H, dd, $J = 10.9$, 2.4 Hz), 7.79 (1H, d, $J = 9.8$ Hz), 7.81 (1H, d, $J = 9.8$ Hz), 7.97 (1H, d, $J = 2.4$ Hz) ppm, HRMS (ESI): *m/z* calcd for $C_{25}H_{16}OF_{13}S$ $[M-H]^-$ 611.0714; found 611.0712.

2-Ethoxy-6-[4-(2-perfluorohexyl)ethylsulfanyl]phenyl]naphthalene (compound **1**-2): 4-[2-(Perfluorohexyl)ethylsulfanyl]bromobenzene (compound **A**) (1.24 g, 2.31 mmol), 6-ethoxy-2-naphthylbronic acid (0.50 g, 2.31 mmol), Na_2CO_3 (0.49 g, 4.63 mmol), $Pd(OAc)_2$ (0.01 g, 2 mol%), and tri(*o*-tolyl)phosphine (0.03 g, 4 mol%) were added in 1,4-dioxane (40 mL) and water (40 mL) in a 200 mL flask, and the mixture was refluxed for 12 h under N_2 atmosphere. The reaction mixture was allowed to cool to room temperature. Then saturated NaCl aqueous solution (100 mL) was added to the mixture, and the resulting solution was extracted with $CHCl_3$ (100 mL × 3). The organic phases were combined and dried with $MgSO_4$, and after filtration, the filtrate was concentrated using a rotary evaporator under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: $CHCl_3$) and recrystallization (EtOH: toluene = 8: 2) to give compound **1**-2 (1.26 g, 2.01 mmol) in 87% yield as colorless powder.: IR (KBr disc): $\nu = 2980$, 2936, $1238-1211\ cm^{-1}$, ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.50$ (3H, t, $J = 7.0$ Hz), 2.40–2.50 (2H, m), 3.12–3.15 (2H, m), 4.17 (2H, q, $J = 6.7$ Hz), 7.17 (1H, d, 2.4 Hz), 7.18 (1H, dd, $J = 10.9$, 2.4 Hz), 7.47 (2H, d, $J = 8.5$ Hz), 7.68 (2H, d, $J = 8.5$ Hz), 7.69 (1H, dd, $J = 10.9$, 2.4 Hz), 7.79 (1H, d, $J = 9.8$ Hz), 7.81 (1H, d, $J = 9.8$ Hz), 7.97 (1H, d, $J = 2.4$ Hz) ppm.

2-Hexyloxy-6-[4-(2-perfluorohexyl)ethylsulfanyl]phenyl]naphthalene (compound **1**-6): 4-[2-(Perfluorohexyl)ethylsulfanyl]bromobenzene (compound **A**) (1.18 g, 2.20 mmol), 6-hexyloxy-2-naphthylbronic acid (0.90 g, 3.30 mmol), Na_2CO_3 (0.63 g, 5.94 mmol), $Pd(OAc)_2$ (0.01 g, 2 mol%), and tri(*o*-tolyl)phosphine (0.03 g, 4 mol%) were added in 1,4-dioxane (40 mL) and water (40 mL) in a 200 mL flask, and the mixture was refluxed for 12 h under N_2 atmosphere. The reaction mixture was allowed to cool to room temperature. Then saturated NaCl aqueous solution (100 mL) was added to the mixture, and the resulting solution was extracted with $CHCl_3$ (100 mL × 3). The organic phases were combined and dried with $MgSO_4$, and after filtration, the filtrate was concentrated using a rotary evaporator under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: $CHCl_3$) and recrystallization (EtOH: toluene = 8: 2) to give compound **1**-6 (0.24 g, 0.132 mmol) in 6% yield as colorless powder: IR (KBr disc): $\nu = 2932$, 2860, $1238-1182\ cm^{-1}$, ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.93$ (3H, t, $J = 6.7$ Hz), 1.38 (2H, quin, $J = 3.7$ Hz), 1.52 (2H, quin, $J = 7.3$ Hz), 1.86 (2H, quin, $J = 7.6$ Hz), 2.40–2.50 (2H, m), 3.12–3.15 (2H, m), 4.09 (2H, t, $J = 6.7$ Hz), 7.17 (1H, d, $J = 2.4$ Hz), 7.18 (1H, dd, $J = 10.9$, 2.4 Hz), 7.47 (2H, d, $J = 8.5$ Hz), 7.68 (2H, d, $J = 8.5$ Hz), 7.69 (1H, dd, $J = 10.9$, 2.4 Hz), 7.79 (1H, d, $J = 9.8$ Hz), 7.81 (1H, d, $J = 9.8$ Hz), 7.97 (1H, d, $J = 2.4$ Hz) ppm, HRMS (ESI): *m/z* calcd for $C_{30}H_{26}OF_{13}S$ $[M-H]^-$ 681.1497; found 681.1497.

Method

The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp = 156.6°C, 28.4 J/g). The DSC thermogram was operated at a heating or cooling rate of 5°C min^{-1}. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). The homogeneous and homeotropic alignments between glass surfaces were achieved by treatment of glass plates with polyimide (Tore SP-810) and cetyltrimethyl ammonium bromide, respectively. ^{1}H NMR spectra were measured using a JEOL JNM-LA500 spectrometer, where tetramethylsilane was used as an internal standard. IR spectra were recorded with a Shimadzu Prestige-21 infrared spectrometer. The purity of the materials was checked by HPLC instead of elemental analysis. Gelation test were achieved as follows. A weighed compound was mixed with an organic solvent in a micro tube (11 mmϕ), and the mixture was heated until the solid dissolved. The resulting solution was cooled to room temperature and then the gelation was checked visually. When upon inversion of the glass tube no fluid ran down the walls of the tube, we judged it “successful gel.” When the gel was formed, we evaluated quantitatively the gel forming ability by determining the MGC, which is the minimum concentration of the compound necessary for gelation at room temperature. Scanning electron microscope (SEM) images were obtained with a JEOL JSM-6510LA. The samples (*i.e.* xerogels) completely removed the organic solvent in *vacuo* were prepared and then were coated with a platinum vapor using autofinecoater (JEOL JFC-1600). A sample was observed by means of secondary electron image (SEI) method operated acceleration voltage of 10 kV.

Results and discussion

Mesomorphic properties for compounds **1**-n were determined by means of DSC measurements and polarized microscope observations.

The DSC thermogram for compound **1**-1 shows endotherms at 144°C, 170°C and 192°C corresponding to the melting, mesophase-mesophase and mesophase–isotropic (I) phase transition phenomena on heating process. The molten material shows exotherm at 189°C, 166°C and 110°C due to the phase transition on a cooling process. The formed textures are shown in Figure 2.

The polarized microscope observation exhibited a typical focal conic fan texture under a homogeneus alignment glass surface and a homeotropic texture (dark under a cross-polarized microscope) on a homeotropic alignment glass surface. A broken-fan texture was observed at 166°C and the homeotropic texture under a homeotropic glass surface on cooling. We can assume that the both mesophases have an orthogonal alignment of the molecule. Therefore, the mesophases are assigned to be smectic A (SmA) and B (SmB) phases.

For compound **1**-6, a similar focal conic fan texture was observed on cooling process from isotropic liquid and the upper mesophase was assigned to be the SmA phase as shown in Figure 3 (a). Lower mesophase for compound **1**-6 also shows a broken fan texture as shown in Figure 3(b), however, the mesophase has a schlieren texture under a homeotropic glass surface, suggesting a smectic C (SmC) phase.

The transition temperatures and latent heats for **1**-n are summarized in Table 1.

The latent heats of compound **1**-1 for the SmB-SmA and SmA–I transitions also support the characterizations, where the value for former transition was determined to be 9.1 kJ mol^{-1} and that for the later was 9.7 kJ mol^{-1}. The similar tendency was observed for compound **1**-2, where the latent heats for the SmB-SmA and SmA-I transitions, that is, 8.6 kJ mol^{-1}

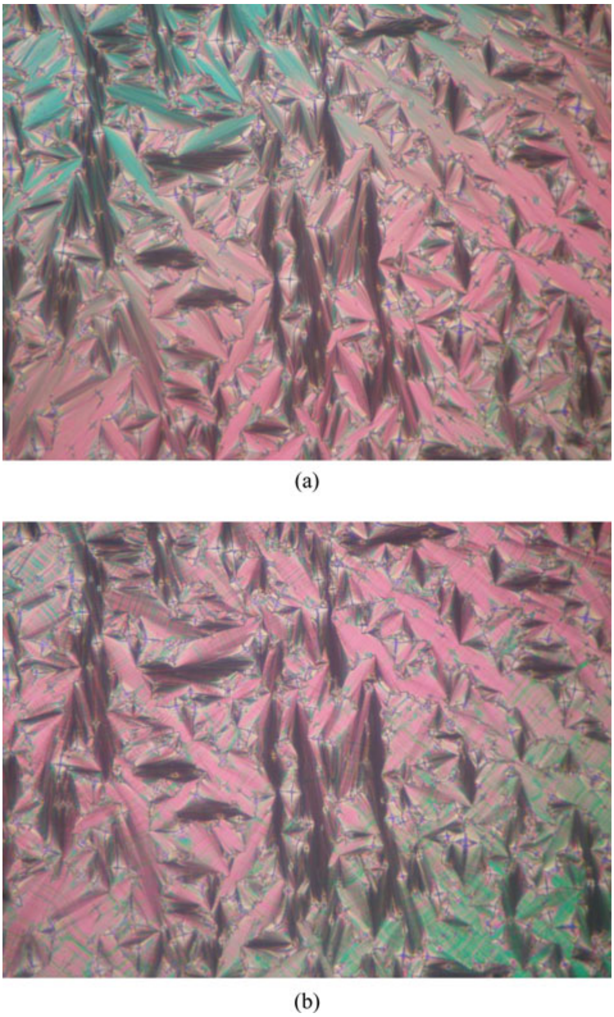


Figure 2. Polarized micrographs for compound **1**-1 (a) at 180°C and (b) at 155°C.

and 11.2 kJ mol^{-1}, respectively. The latent heat for the SmA–I transition of compound **1**-6 is determined to be 9.6 kJ mol^{-1}, which is similar to that for compounds **1**-1 and **1**-2. On the other hand, the latent heat for the lower smectic phase-SmA transition is determined to be 0.1 kJ mol^{-1}, which is too small to assign to be the SmB-SmA transition. The small value of the latent heat for the smectic-SmA transition also supports that the lower smectic phase assigned to be the SmC phase.

Interestingly, compounds **1**-n formed a physical gel (i.e. thermo-reversible gel) in several organic solvents. Therefore, we carried out the gelation test of compounds **1**-1 and **1**-6 in several organic solvents.

Table 2 shows the results of the gelation test for compounds **1**-1 and **1**-6 in several organic solvents. Compound **1**-1 formed gels in *n*-octane, toluene, ethanol, 1-octanol, acetonitrile, γ-butyrolactone (GBL) and proprylene carbonate (PC), where the minimum gel concentrations were 0.6, 5.0, 0.5, 0.6, 0.4, 0.2 and 0.4 wt%, respectively, while precipitated in *N,N*-dimethylformamide (DMF).

On the other hand, compound **1**-6 was soluble in toluene and formed gel in the other solvents at similar concentrations as shown in Table 2. The results suggest that gelation ability

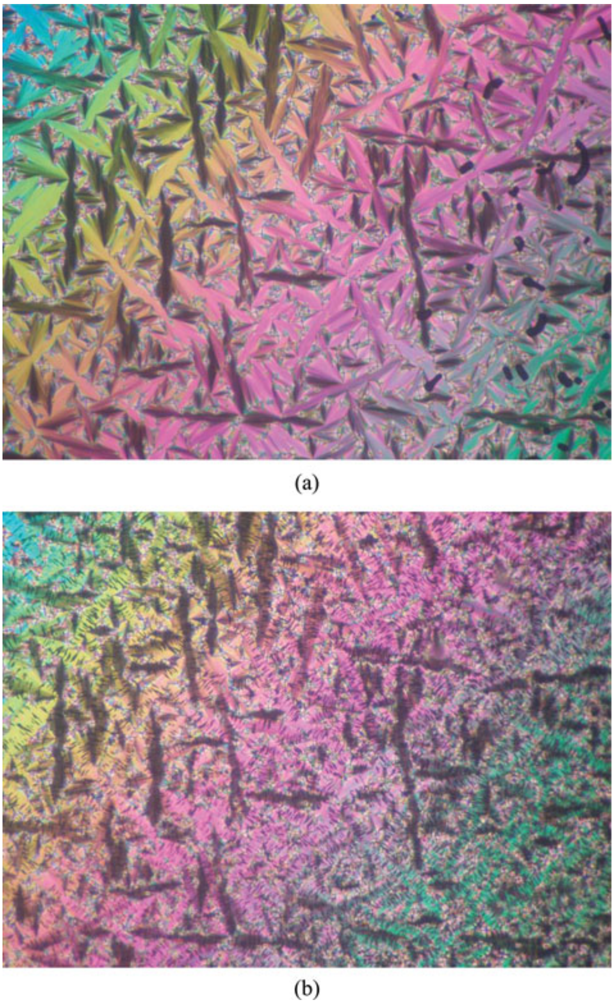


Figure 3. Polarized micrographs for compound **1**-6 (a) at 145°C and (b) at 130°C.

for compounds **1**-n is an independent of an alkyl chain length in the terminal position of the molecule. The sol-gel transition temperatures for the PC gels are plotted against the concentration of compounds **1**-1 and **1**-6 as shown in Figure 4.

The sol-gel transition temperatures for the PC gels increased with increasing the concentration of compounds **1**-1 and **1**-6. For compound **1**-1, the sol-gel transition temperature is ca. 60°C in more than 1wt% of the concentration. The sol-gel transition temperatures for compound 1–6 are higher than those for compound **1**-1, where the temperature is ca. 80°C at

Table 1. Transition temperatures for compounds **1**-n.

	Transition temperatures (°C)								Latent heats (kJ mol^{-1})			
Compounds	C		SmB		SmC	SmA		I	mp	SmB–SmA	SmC–SmA	SmA–I
1-1	●	144	●	170	—	●	192	●	20.8	9.1	5.2	9.7
1-2	●	153	●	171	—	●	203	●	20.2	8.6	8.3	11.2
1-6	●	140	—		(● 134)	●	171	●	20.1		(0.1)	9.6

C, SmB, SmC, SmA and I indicate crystal, smectic B, smectic C, and smectic A and isotropic phases, respectively. Parentheses indicate a monotropic transition.

Table 2. Minimum gel concentration for compounds **1**-1 and **1**-6.

	Compounds (concentration, wt%)[a]	
Solvents	**1**-1	**1**-6
n-Octane	G (0.6)	G (0.8)
Toluene	G (5.0)	S (5.0)
Ethanol	G (0.5)	G (0.8)
1-Octanol	G (0.6)	G (1.0)
Acetonitrile	G (0.4)	G (0.8)
DMF	P (5.0)	G (0.5)
PC[b]	G (0.2)	G (0.4)
GBL[c]	G (0.4)	G (0.4)

[a] G, S and P are gel, sol and precipitated states, respectively. [b] PC: Propylene carbonate, [c] GBL: γ-Butyrolactone.

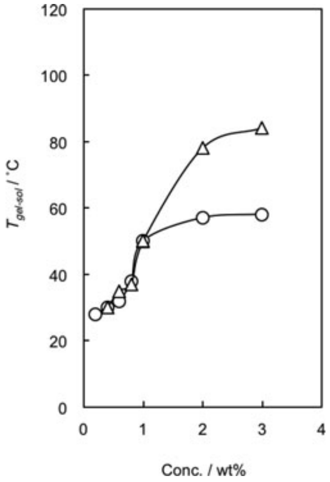


Figure 4. Plots for sol-gel transition temperature of propylene carbonate gel against concentration of compounds **1**-1 (circle) and **1**-6 (triangle).

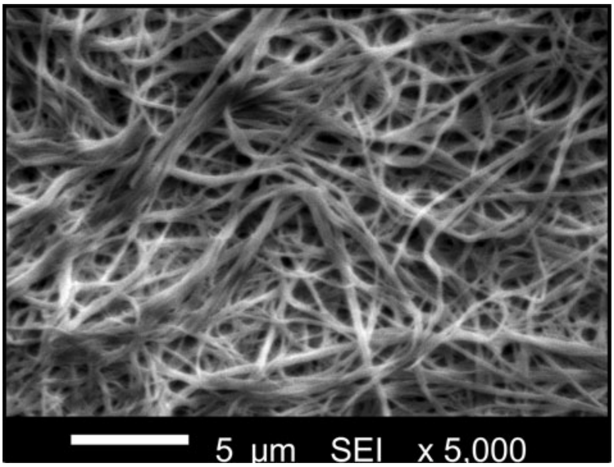


Figure 5. SEM image for xerogel prepared from propylene carbonate gel (x5,000).

3 wt% of compound **1**-6. These results indicate that the terminal alkyl chain has an important influence on the sol-gel transition temperature.

The gelation phenomena are also confirmed using scanning electron microscope (SEM) observation, and the result for a xerogel prepared from propylene carbonate gel containing 3 wt% compound **1**-6 is shown in Figure 5. It is apparent from the figure that the gel consists of several rod-like fibers and the fibers are aligned to form the network structures with diameters of less μm order.

In conclusion, intermolecular interaction around the terminal alkyl group acts an impotant role for displaying the mesomorphic property and gelation ability. The perfluorohexylethyl group is also indispensable for the gelation ability. The present results will provide an important information for mesomorphic and gelation phenomena.

Further examination is now underway, and the results will be published elsewhere.

Funding

This work is partly supported by Industrial Technology Research Grant Program in 2006 from New Energy and Industrial Technology Development Organization (NEDO) of Japan, TEPCO Memorial Foundation and The Fujikura Foundation.

References

[1] Terech, P., & Weiss, R. G. (1997). *Chem. Rev.*, *97*, 313.
[2] Babu, S. S., Praveen, V. K., & Ajayaghosh, A. (2014). *Chem. Rev.*, *114*, 1973.
[3] Morita, Y., Kawabe, K., Zhang, F., Okamoto, H., Takenaka, S., & Kita, H. (2005). *Chem. Lett.*, *34*, 1650.
[4] Morita, Y., Ushijima, H., Era, K., Kasatani, K., & Okamoto, H. (2008). *Mol. Cryst. Liq. Cryst.*, *494*, 282.
[5] Hird, M. (2007). *Chem. Soc. Rev.*, *36*, 2070.
[6] Okamoto, H., Murai, H., & Takenaka, S. (1997). *Bull. Chem. Soc. Jpn*, *70*, 3165.
[7] Okamoto, H., Yamada, N., & Takenaka, S. (1998). *J. Fluorine Chem.*, *91*, 125.
[8] Duan, M., Okamoto, H., Petrov, V. F., & Takenaka, S. (1999). *Bul. Chem. Soc. Jpn*, *72*, 1637.
[9] Duan, M., Okamoto, H., Petrov, V. F., & Takenaka, S. (1998). *Bull. Chem. Soc. Jpn*, *71*, 2735.
[10] Yano, M., Taketsugu, T., Hori, K., Okamoto, H., & Takenaka, S. (2004). *Chem., Eur. J.*, *10*, 3991.
[11] Ajayaghosh, A., & George, S. J. (2001). *J. Am. Chem. Soc.*, *123*, 5148.
[12] Bujanowski, V. J., Katsoulis, D. E., & Ziemelis, M. J. (1994). *J. Mater. Chem.*, *4*, 1181.
[13] Sato, H., Yajima, T., & Yamagishi, A. (2011). *Chem. Commun.*, *47*, 3736.
[14] Pugh, C., Höpken, J., & Möller, M. (1988). *Polym. Prep.*, *29*, 460.
[15] Cao, B., Kaneshige, Y., Matsue, Y., Morita, Y., & Okamoto, H. (2016). *New J. Chem.*, *40*, 4884.
[16] Cao, B., Hayashida, S., Morita, Y., & Okamoto, H. (2016). *Mol. Cryst. Liq. Cryst.*, *632*, 49.
[17] Yoshida, T., Hirakawa, T., Nakamura, T., Yamada, Y., Tatsuno, H., Hirai, M., Morita, Y., & Okamoto, H. (2015). *Bull. Chem. Soc. Jpn*, *88*, 1447.
[18] Yoshida, T., Nakamura, T., Morita, Y., & Okamoto, H. (2015). *Chem. Lett.*, *44*, 512.