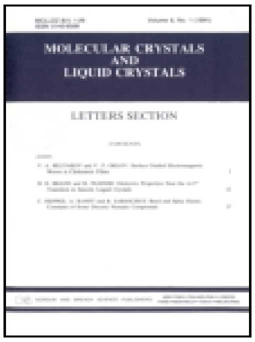

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Synthesis, liquid crystal property and gelation ability of semi-fluorinated 4-alkoxyphenyl 4-alkoxybenzoates

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ABSTRACT
This paper describes the synthesis and physico-chemical properties for 4-(4-perfluorohexylbutoxy)phenyl 4-alkoxybenzoate (compounds **1**-n), and the results are compared with the corresponding hydrocarbon derivatives (compounds **2**-n). Compounds **1**-n show exclusively a smectic A (SmA) phase, where the SmA–isotropic phase transition temperatures are 142°C for **1**-1 and 147°C for **1**-6. The SmA phase is characterized using a polarized microscope and DSC measurements. Interestingly, compound **1**-6 forms gels in *n*-octane, ethanol, and aprotic polar solvents such as acetonitrile and γ-butyrolactone, while compound **1**-1 shows no-gelation ability. The *n*-octane 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

Self-assemble phenomena are of much attention, especially for their application to nanomaterials such as liquid crystal (LC) materials and organic gelators. [1–4] A lot of researches and applications have been reported on the molecular structure and mechanism of the molecular aggregation. Many LC materials have been reported up to now, where a rigid core and flexible terminal alkyl chain(s) are indispensable for exhibiting 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 reported, however, new organic gelators were often discovered accidentally, and the researches are devoted to understanding 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].

Several organic gelators having perfluoroalkyl chains were also prepared and it has been clarified that the perfluoroalkyl chains affect the gelation ability differently from the alkyl chains [13–15]. In our earlier papers, we have reported that 4-(2-perfluorooctyl)ethoxy and

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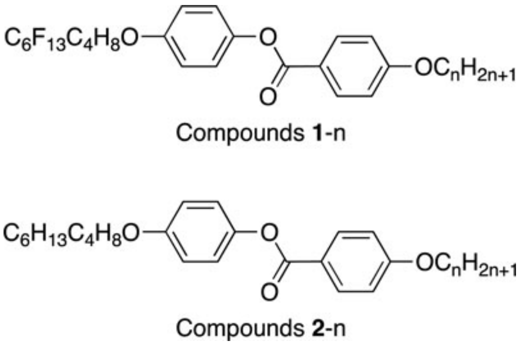


Figure 1. Chemical structure for compounds **1**-n.

4-(2-perfluorooctyl)ethylthio group affect their mesomorphic properties and gelation ability [16,17]. Furthermore, we have also investigated some organic gelators having perfluoroalkyl chains at the both terminal positions of the molecule [18,19].

This paper describes synthesis and physico-chemical properties of LC materials and organic gelators, 4-(4-perfluorohexylbutoxy)phenyl 4-alkoxybenzoates (compounds **1**-n) and the corresponding hydrocarbon derivatives (4-decyloxyphenyl 4-alkoxybenzoates, compounds **2**-n) shown in Figure 1. The molecular characteristics are to incorporate neither protic function group nor so long hydrocarbon chain. The chemical structure is simple, and similar to the conventional LC materials. The experimental results are discussed in terms of the molecular structure.

Experimental

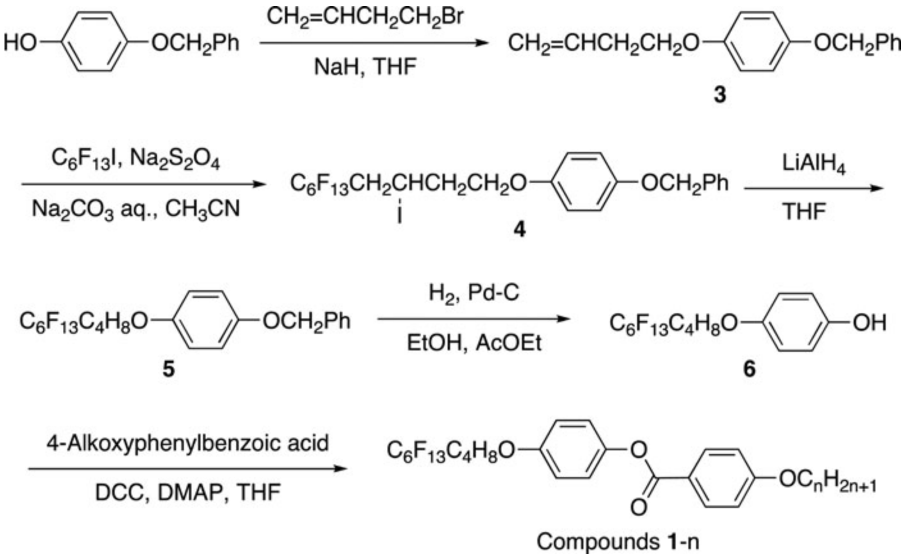
Materials

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 the synthetic procedures are as follows.

1-(Benzyloxy)-4-(but-3-enyloxy)benzene (**3**): To a suspended solution of 4-benzyloxyphenol (20 g, 0.1 mol) and NaH (6.0 g, 0.15 mol) and catalytic amount of KI in THF (50 ml) was added 4-bromobut-1-ene (20.25 g, 0.15 mol), and the mixture was refluxed for 3 days. The reaction mixture was then cooled to room temperature, and quenched with H_2O. The reaction mixture was extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and removed in vacuo. The residue was purified by silica gel chromatography, and then recrystallized from ethanol to give compound **3**, as a colorless solid (7.0 g, yield: 27%), mp = 50–52°C.

IR and ^{1}H NMR spectra for compound **3**: IR (KBr disc) $\nu = 3083, 2983, 2945, 2906, 2862, 1508$, and 1290 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta = 2.57$ (2H, qd, $J = 6.8, 1.2$ Hz), 4.00 (2H, td, $J = 6.8, 0.8$ Hz), 5.05 (2H, s), 5.15 (1H, d, $J = 10.0$ Hz), 5.21 (1H, d, $J = 17.2$ Hz), 5.90–6.00 (1H, m), 6.88 (2H, d, $J = 8.4$ Hz), 6.95 (2H, d, $J = 8.4$ Hz,), and 7.34–7.48 (m, 5H), ppm.

1-(Benzyloxy)-4-(3-iodo-4-perfluorohexylbutoxy)benzene (**4**): To a mixture of compound **3** (7.0 g, 27.5 mmol), sodium hydrogen carbonate (2.3 g, 27.5 mmol), and sodium hydrosulfite (4.8 g, 27.5 mmol) in a mixed solvent of CH_3CN (30 ml) and H_2O (20 ml) was added perfluorohexyl iodide (12.3 g, 27.5 mmol) and the reaction mixture was stirred under shielded light for overnight. The reaction mixture was diluted with ethyl acetate and washed with



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

H_2O twice, dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo. The residue was recrystallized from ethanol to give compound **4**, as a colorless solid (11.2 g, yield: 58%), mp = 68–72°C. Compound **4** has a mesomorphic property and the details will be published elsewhere.

IR and ^1H NMR spectra for compound **4**: IR (KBr disc) $\nu = 1512$ and $1242\ cm^{-1}$. ^1H NMR ($CDCl_3$) $\delta = 2.46$–2.60 (2H, m), 3.96 (2H, t, $J = 6.7$ Hz), 5.01 (2H, s), 5.09–5.18 (2H, m), 5.91 (1H, m), 6.84 (2H, d, $J = 8.4$ Hz), 6.90 (2H, d, $J = 8.4$ Hz), and 7.32–7.42 (5H, m) ppm.

1-(Benzyloxy)-4-(4-perfluorohexylbutoxy)benzene (**5**): To a solution of compound **4** (11.2 g, 16 mmol) in THF (100 ml) was added $LiAlH_4$ (1.2 g, 32 mmol) portionwise, and the reaction mixture was stirred overnight. The reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and the solvent was removed in *vacuo*. The residue was purified by silica gel chromatography, and then recrystallized from ethanol to give compound **5**, as a colorless solid (3.6 g, yield: 39%), mp = 68–77°C. Compound **5** has a mesomorphic property and the details will be published elsewhere.

IR and ^1H NMR spectra for compound **5**: IR (KBr disc) $\nu = 1512$ and $1242\ cm^{-1}$. ^1H NMR ($CDCl_3$) $\delta = 1.79$–1.97 (4H, m), 2.09–2.20 (2H, m), 3.94 (2H, t, $J = 5.7$ Hz), 5.01 (2H, s), 6.82 (2H, d, $J = 8.4$ Hz), 6.90 (2H, d, $J = 8.4$ Hz), and 7.31–7.42 (5H, m) ppm.

4-(4-Perfluorohexylbutoxy)phenol (**6**): Under hydrogen atmosphere, a mixture of compound **5** (3.5 g, 6.2 mmol) and Pd-C (0.1 g) in a mixed solvent of ethanol (150 ml) and ethyl acetate (150 ml) was vigorously stirred. After the reaction completed, the reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was recrystallized from toluene to give compound **6**, as a colorless solid. (1.76 g, yield: 66%), mp = 72–74°C.

IR and ^1H NMR spectra for compound **6**: IR (KBr disc) $\nu = 3460$, 1512 and $1242\ cm^{-1}$. ^1H NMR ($CDCl_3$) $\delta = 1.78$–1.88 (4H, m), 2.09–2.27 (2H, m), 3.94 (2H, t, $J = 5.8$ Hz), 4.77 (1H, s), and 6.79 (4H, s) ppm.

General procedure to prepared compounds **1**-n and **2**-n: Compounds **1** and **2** were prepared by conventional esterification (DCC method in THF) with compound **6** for compounds **1** or 4-decyloxyphenol for compounds **2** and the corresponding 4-alkoxybenzoic acid. The products were purified by silica gel chromatography, and then recrystallized from ethanol. The spectra data are as follows.

IR and ^{1}H NMR spectra for compound **1**-1: IR (KBr disc) $\nu = 1730$, 1512, and 1201 cm^{-1}. ^{1}H NMR (CDCl$_3$) $\delta = 1.80$–1.92 (4H, m), 2.12–2.23 (2H, m), 3.90 (3H, s), 4.01 (2H, t, $J = 5.8$ Hz), 6.92 (2H, d, $J = 8.5$ Hz), 6.98 (2H, d $J = 9.2$ Hz), 7.11 (2H, d, $J = 9.2$ Hz), and 8.15 (2H, d, $J = 8.5$ Hz) ppm.

IR and ^{1}H NMR spectra for compound **1**-6: IR (KBr disc) $\nu = 1724$, 1521, and 1202 cm^{-1}. ^{1}H NMR (CDCl$_3$) $\delta = 1.80$–1.92 (4H, m), 2.12–2.23 (2H, m), 4.01 (2H, t, $J = 5.8$ Hz), 6.92 (2H, d, $J = 9.2$ Hz), 6.98 (2H, d, $J = 8.5$ Hz), 7.11 (2H, d, $J = 9.2$ Hz), and 8.14 (2H, d, $J = 8.5$ Hz) ppm.

Method

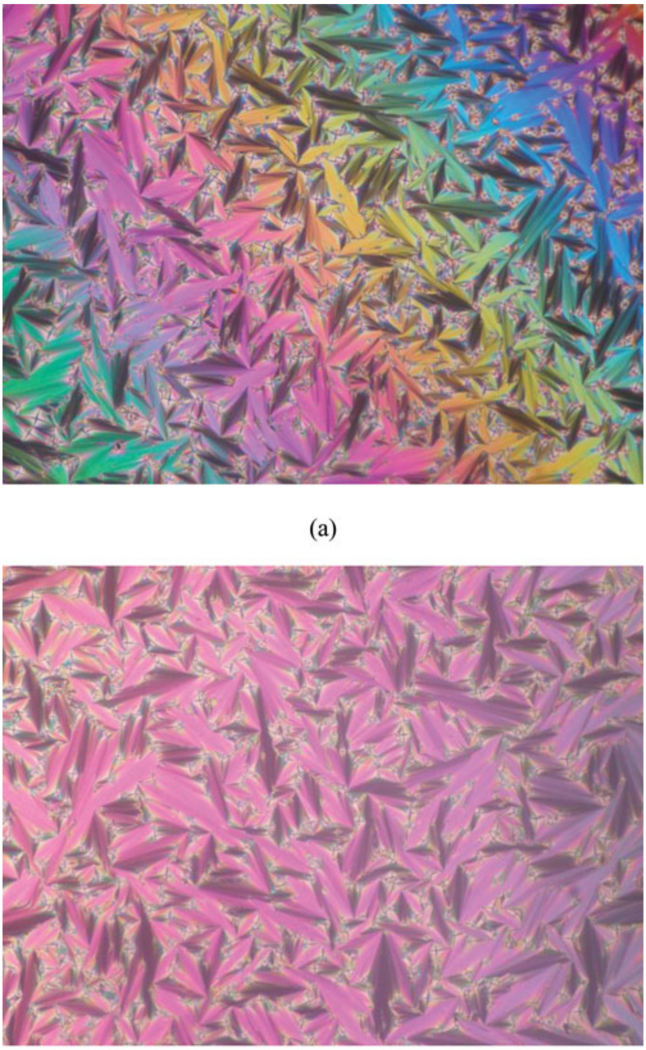
The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp = 156.6°C, 28.4 J/g). The DSC thermogram was operated at a heating or cooling rate of 5°C min^{-1}. The mesophases were characterized using a Nikon POH 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 and DSC thermograms using a 'DSCPURITY' program (SII instrument) 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 and **2**-n were determined by means of DSC measurements and polarized microscope observations.

The DSC thermogram for compound **1**-1 shows endotherms at 96°C and 142°C corresponding to the melting and mesophase–isotropic (I) phase transition phenomena on heating process. The molten material shows a small exotherm at 138°C due to the phase transition during a cooling process. The formed texture is shown in Figure 2 (a). The polarized microscope observation exhibited a typical focal conic fan texture on a homogeneus glass surface.

For compound **1**-6, a similar focal conic fan texture was also observed on cooling process as shown in Figure 2 (b). We can assume that the mesophases have an orthogonal alignment of the molecule, since the mesophases showed a typical homeotropic texture (dark under a cross-polarized microscope) on a homeotropic alignment glass surface. Therefore, the mesophases



(a)

(b)

Figure 2. Polarized micrographs for (a) compound **1**-1 at 130°C and (b) compound **1**-6 at 130°C.

was assigned to be a smectic A (SmA) phase. For compound **2**-1, a schlieren texture was observed on cooling process and the mesophase was assigned to be a nematic (N) phase as shown in Figure 3.

The transition temperatures and latent heats for **1**-n and the corresponding hydrocarbon derivatives (compounds **2**-n) are summarized in Table 1.

The latent heats for the SmA–I transition also support the characterization, where the value for compound **1**-1 was determined to be 5.2 kJ mol^{-1} and that for **1**-6 was 8.3 kJ mol^{-1}. The SmA–I transition temperatures for **1**-n increase slightly on increasing the carbon number, while the melting points decrease. The thermal stability of mesophase for compounds **1**-n is higher ca. 70°C than that for compounds **2**-n, while melting point is slightly high, indicating the thermal range of the mesophase for compounds **1**-n are wider than that for compounds **2**-n. The thermal tendency is frequently seen LC materials having a perfluoroalkyl chain [5].

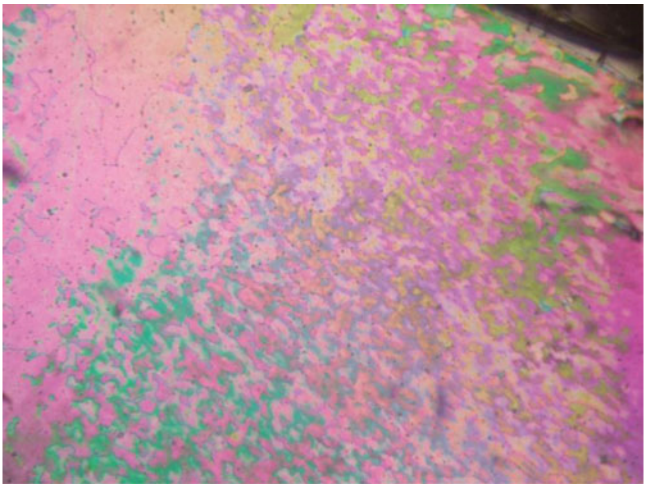


Figure 3. Polarized micrograph for compound **2**-1 at 70°C.

Table 1. Transition temperatures for compounds **1**-n and **2**-n.

	Transition temperatures (°C)									Latent heats (kJ mol^{-1})			
Compounds	C		SmC		SmA		N		I	mp	SmC–N	SmA–I	N–I
1-1	•	96	—		•	142	—		•	40.6	—	5.2	—
1-6	•	77	—		•	147	—		•	30.6	—	8.3	—
2-1	•	71	—		—		•	73	•	45.3	—	—	1.3
2-6[1)]	•	61	(•	55)	—		•	87	•	48.5	1.9	—	1.8

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

1) Transition temperatures are cited from ref. [20].

Interestingly, compound **1**-6 formed a physical gel (i.e. thermo-reversible gel) in several organic solvents as shown in Figure 4. Therefore, we carried out the gelation test of compounds **1**-n and **2**-n in several organic solvents.

Table 2 shows the results of the gelation test for compounds **1**-n and **2**-n in several organic solvents. Compound **1**-6 formed gels in *n*-octane, ethanol, acetonitrile, and γ-butyrolactone (GBL), where the minimum gel concentrations were 3.5, 2.5, 5.0, and 4.5wt%, respectively. On the other hand, compound **1**-1 was precipitated in *n*-octane, ethanol, 1-octanol, propylene carbonate, and GBL at 5wt%.

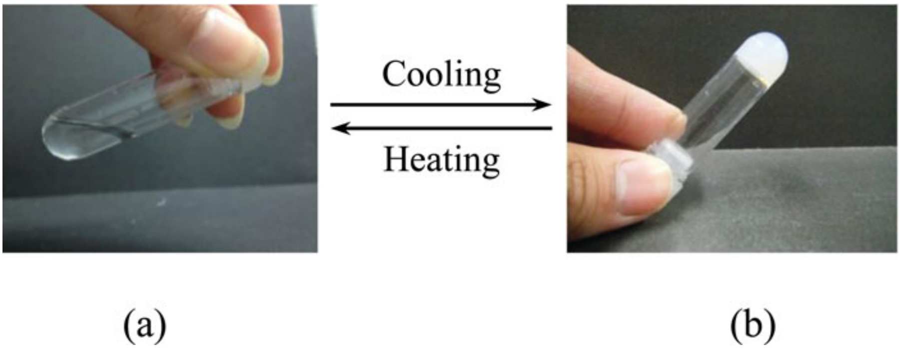


Figure 4. Photographs for physical gel (thermo-reversible gel); (a) sol state, (b) gel state.

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

	Compounds (concentration, wt%) [a]			
Solvents	**1**-1	**1**-6	**2**-1	**2**-6
n-Octane	P (5.0)	G (3.5)	P (5.0)	P (5.0)
Toluene	S (5.0)	S (5.0)	S (5.0)	S (5.0)
Ethanol	P (5.0)	G (2.5)	P (5.0)	P (5.0)
1-Octanol	P (5.0)	P (5.0)	P (5.0)	P (5.0)
AcOEt	S (5.0)	S (5.0)	S (5.0)	S (5.0)
Acetonitrile	S (5.0)	G (5.0)	P (5.0)	P (5.0)
PC [b]	P (5.0)	P (5.0)	P (5.0)	P (5.0)
GBL [c]	P (5.0)	G (4.5)	P (5.0)	P (5.0)

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

On the other hand, compounds **2**-1 and **2**-6 were precipitated or soluble in the examined solvents as shown in Table 2. These results indicate that both of a semi-perfluoroalkyl chain and a subtle long alkyl chain in the molecular structure are indispensable to form the organic gels.

Figures 5 shows a photograph of organic gels (GBL, acetonitrile, ethanol, and *n*-octane gels) formed by compound **1**-6 at room temperature on cooling from an isotropic liquid state, and the gels are cloudy.

The gelation phenomena are also confirmed by means of scanning electron microscope (SEM) observation, and the result for a xerogel prepared from *n*-octane gel is shown in Figure 6. It is apparent from the figure that the gel consists of several rod-like fibers aligned to form the network structures with bundles with diameters of less μm order.

In conclusion, intermolecular interaction around the semi-perfluoroalkyl group acts an impotant role for displaying the mesomorphic property and gelation ability. The terminal subtle long alkoxy group is also indispensable for the gelation ability. The present results should provide an important information for mesomorphic and gelation phenomena.

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

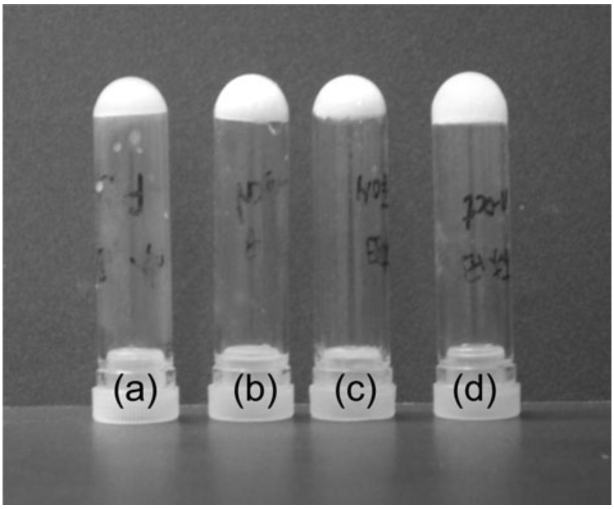


Figure 5. Photographs for organic gels formed by compound **1**-6; (a) γ-butyrolactone gel (4.5wt%), (b) acetonitrile gel (5.0wt%), (c) ethanol gel (5.0wt%), (d) *n*-octane gel (3.5wt%).

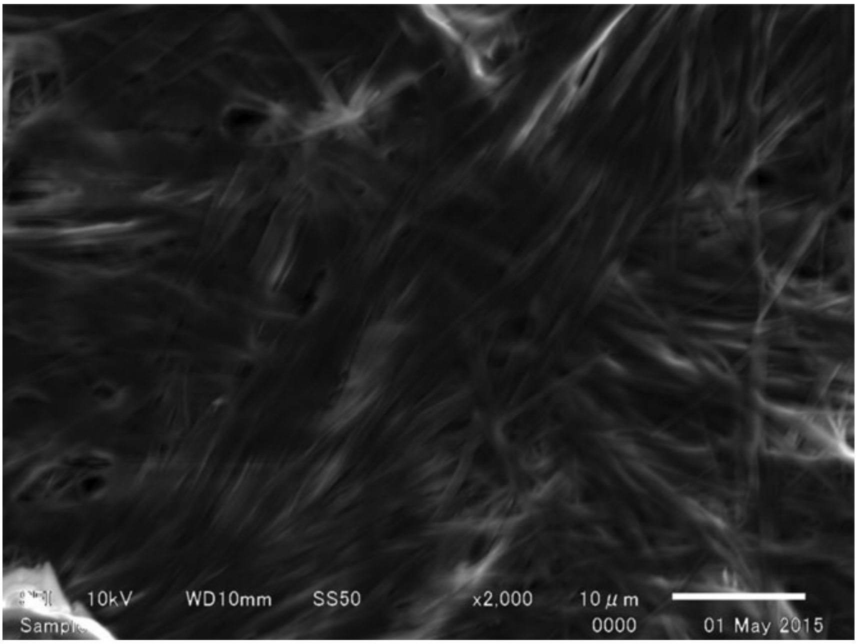


Figure 6. SEM image for xerogel prepared from *n*-octane gel (x2,000).

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