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공학석사학위논문

Dispersion of SWNTs by an Oligothiophene-based Organogelator

올리고사이오펜 유기젤에 의한 단일벽 탄소 나노튜브의 분산

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이 논문을 공학석사학위논문으로 제출함

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재료공학부

박 민 영

박민영의 석사학위논문을 인준함

2013년 2월

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Abstract

We prepared organogels of an oligothiophene-based organogelator and their composites with SWNTs. As CNTs have high aspect ratios and extraordinary electrical, chemical and mechanical properties, they have diverse potential applications. However, their practical applications remain limited because CNTs predominantly exist in an aggregated state due to the *van der Waals* force between themselves. In this work, SWNTs were dispersed in an organogel using an oligothiophene-based organogelator as a dispersant. The organogelator was prepared by imine condensation between the oligothiophene unit having aldehyde end groups and benzamide derivatives having long alkyl chains. A SWNTs/Gel composite was prepared by mixing SWNTs in a gelator solution. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) studies confirmed that SWNTs were well dispersed in organogel due to strong π-π interaction between oligothiophenes and SWNTs. In the rheological study, SWNTs/Gel composite showed enhanced dynamic mechanical properties, conductivity compared with the organogel

Keywords: **organogel, carbon nanotubes, oligothiophenes, composites, dispersion, self-assembly**

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CONTENTS

1. Introduction

Carbon nanotubes (CNTs) are one of the most prospective materials in many applications of nanotechnology such as fuel cell, water purification, solar cell, supercapacitor, and nano-reactor.[1-5] Due to the extraordinary mechanical, electrical and structural properties of CNTs, a number of researches about their properties and applications have been studied for decades.

CNTs have cylindrical structure with a high aspect ratio and consist of only sp^2 bonds to induce excellent electrical property.[6] Also they have good thermal conductivity and unique optical property.[7-10] Although they have excellent properties, it is not easy to use them in many applications. Because of strong *van der Waals* force between CNTs, they are easily aggregated and have very low solubility to make process difficult.[11] Many researchers have investigated to improve the solubility of CNTs[10] via covalent modification and non-covalent modification. In case of covalent modification, one of the typical example is formation of carboxylic groups and other oxygenated groups under strong acidic condition.[12] The carboxylic groups on the CNT surfaces can be substituted for different chemical groups,[13] and also give CNTs a hydrophilic character which makes them soluble in several solvents, even in the water.[16-18] But, a harsh condition for modification can destroy conjugated bonds of its surfaces, and decrease inherent properties of CNTs. On the other hand, non-covalent modification can preserve electrical and mechanical properties of

CNTs. Dispersants such as surfactant, polymer, liquid crystal, ionic liquid, hydrogel and organogel which can interact with CNTs by physical interaction are used for this modification.[14-15] Various kinds of dispersants were proved to increase dispersibility of CNTs by using π-π stacking, hydrogen bonding and ionic interaction, etc.

Organogels which are thermoreversible materials are formed by the self-assembly of low-weight organic molecules, organogelators. Each molecule aggregates into one-dimensional assemblies, which form the whole organogel structure as a three-dimensional network. To make organogels, organogelators are dissolved in the solvent, and heated, then cooled down under the sol-gel transition temperature. During the cooling process, solvent molecules are captured inside the network structure of organogelators. Although organogels mostly consist of liquid, these systems show similar appearances, and rheological behaviors of solids. For this reason, organogel systems have been paid great attention in various areas such as drug delivery system[22], chemosensor[23], water purification[24] and organic electronics.[25-32]

There are a few papers related an organogel as a dispersant for CNTs.[19-20] Asish et al. prepared organogel- CNTs composite, which incorporated SWNTs into the gel formed by a low molecular mass organogelator based on L-alanine.[21] Interestingly, using near IR laser irradiation at 1064 nm for a short duration time at room temperature, it was possible to cause a gel-to-sol phase transition of the composites selectively. However, long irradiation of the organogel under same condition did not cause gel melting. It suggested that this novel organogel-CNTs composite showed thermo-responsive behavior caused by near IR irradiation.

Owing to low band gap energy, high charge mobility and conductivity, oligothiophene derivatives have been studied for organic electronic applications such as organic solar cell, field-effect transistors, fluorescent probe, electroluminescent devices, diodes, batteries and chemical sensors.[33] Also oligothiophene derivatives performed as an excellent organogelator for a variety of organic solvents and showed the thermochromic property during the sol-gel transition. There are only a few reports of oligothiophene-based gelator, because oligothiophenes have much lower solubility than monomeric or dimeric thiophenes, although at least four to six thiophenes units are needed for charge transport.

Kawano et al. prepared a series of oligothiophene organogelators which bear two cholesteryl groups and investigated unique thermochromic property.[34] It was found that color change was induced by the conformation change through the sol-gel transition. These gelators self-assembled into 1D fiber structure by π-π stacking (H-aggregation mode).

Pampa et al. studied the morphology and electrical property of oligothiophene super-gelator with PCBM (Phenyl-C_{61}-butyric acid methyl ester).[35] PCBM is commonly used for n-type semiconductors, and its blends with electron donor materials are well-known as materials used in organic solar cell. In the blend of oligothiophene with PCBM, atomic force microscopy (AFM) study confirmed that PCBM did not interrupt self-assembly process of oligothiophene organogeletor. Moreover the mobility of oligothiophene derivatives had no significant differences with reported value of polythiophene owing to the similar π-π stacking between self-assembled oraganogelator.

Stone et al. prepared quaterthiophene and quinquethiophene derivatives containing amide groups.[33] They studied H-bonding and π-π stacking between the molecules which helped to form 1D nanofiber structure in various organic solvents. In case of the electrical properties, only quinquethiophene derivative showed high conductivity. While a device was exposed to UV light, the current increased, showing that the quinquethiophene derivatives assembled into 1D nanofiber enabled charge transport.

Herein we synthesized a new oligothiophene-based organogelator and made organogel composites with SWNTs. A rigid oligothiophene core was introduced to gelator molecule to induce strong interaction between the gelator and SWNTs. Properties of organogels and SWNTs/Gel composites were investigated in various ways. The oligothiophene-based organogelator showed good gelation property in alkane solvents, such as *n*-decane and *n*-hexane. The scanning electron microscopy (SEM) and high resolution transmission electron microscopy (TEM) study showed that SWNTs were well-dispersed in the organogel. We compared rheological properties and electrical resistivity of the gels with those of SWNTs/Gel composites to investigate the effect of SWNTs incorporation.

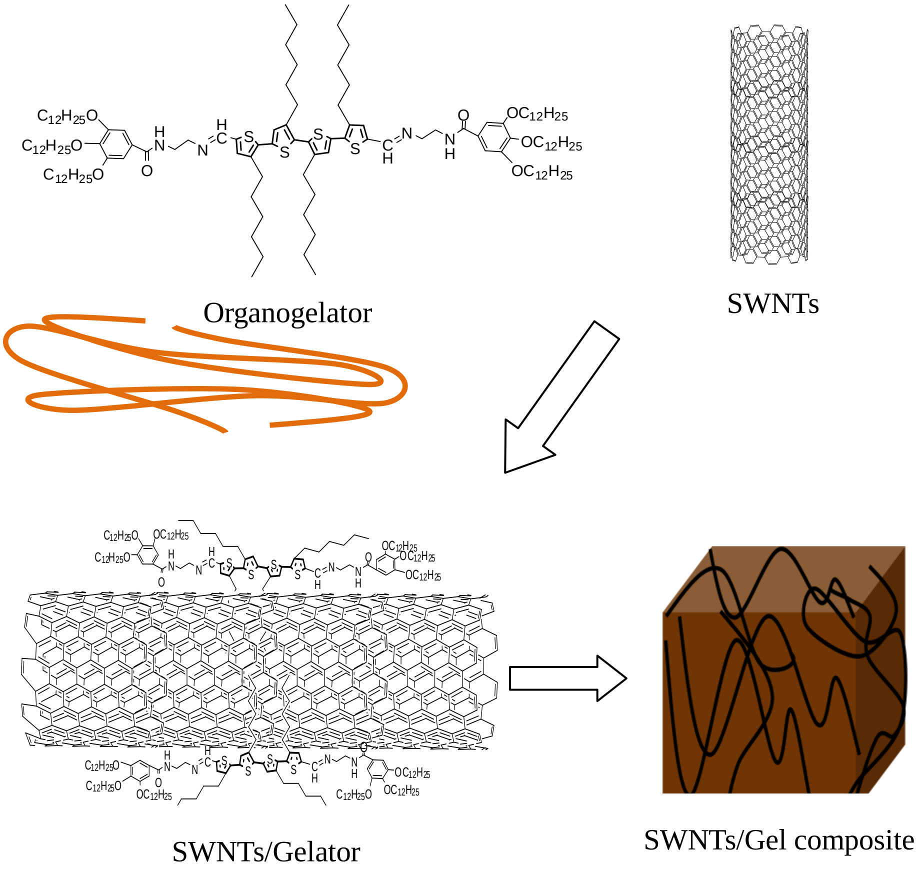


Figure 1. Schematic drawing of incorporating SWNTs into the organogel.

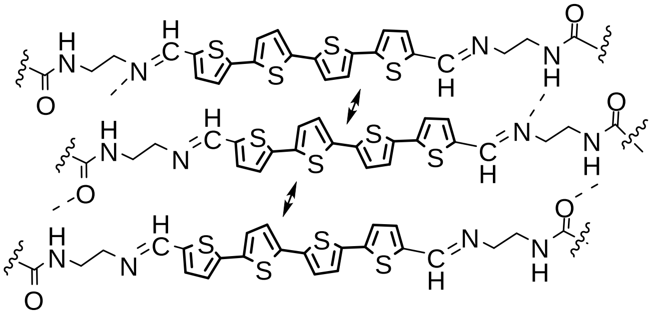


Figure 2. Proposed self-assembly structure of the organogelator molecules.

2. Experimental

2.1. Materials

Methyl 3,4,5-trihydroxybenzote, 1-bromododecane, ethylenediamine, *N*-bromosuccinimide (NBS), (benzotriazol-1-yloxy) tripyrrolidinophosphonium hexafluorophosphate (PyBOP), phosphorus (V) oxychloride, 2,2′-bipyridyl, 1,5-cyclooctadiene, *n*-decane, and sodium acetate were purchased from Aldrich. 3, 4’-dihexyl-2,2’-bithiophene was purchased from TCI. Bis (1, 5-cyclooctadiene) nickel (0) was purchased from Alfa aesar. Potassium carbonate, potassium hydroxide, magnesium sulfate, hydrochloric acid (35 wt%), and diethyl ether were purchased from Daejung Chemical & Metals Co.. *N*,*N*-Dimethylformamide (DMF), *n*-hexane, ethyl acetate, ethanol, acetic acid, tetrahydrofuran, dichloromethane and chloroform were purchased from Junsei and used without further purification. Prinstine single-walled carbon nanotubes (SWNTs) were purchased from Hanhwa Nanotech (ASP-100T, synthesized by arc-discharge method). Silica gel (Merck 60) was used for column chromatography. THF was distilled with sodium before use. DMF was distilled with magnesium sulfate before use.

2.2. Characterization

2.2.1. Nuclear magnetic resonance spectroscopy

^{1}H and ^{13}C NMR spectra were recorded by Bruker Avance 300 (300 MHz) and Bruker Avance 500 (125 MHz) spectrometer, respectively.

2.2.2. Infrared spectroscopy

Fourier transform infrared (FT-IR) spectra were performed with a Perkin–Elmer Spectrum GX I instrument using KBr pellets. When characterizing the SWNTs/Gel composite, the SWNTs were sonicated in the organogelator solution for 10 min, and then dried at room temperature. The gel was dried at a reduced pressure overnight before processing into pellets.

2.2.3. Elemental analysis

Elemental analysis was obtained by a CE Instrument Flash 1112 elemental analyzer at the National Center for Inter-University Research Facilities of Seoul National University.

2.2.4. Ultraviolet-Visible spectroscopy

UV-Vis spectra were recorded by a SCINCO S-3150 instrument. When characterizing SWNTs/gelator solution, the SWNTs were sonicated in the organogelator solution (3.0×10^{-5} M) for 1 h before measurement.

2.2.5. Photoluminescence spectroscopy

Photoluminescence spectra were obtained from Shimadzu RF-5301 PC spectrofluorometer. The organogelator molecules were dissolved in *n*-decane and tetrahydrofuran, as 3.0×10^{-5} M concentration. When measuring SWNTs/gelator solution, SWNTs were sonicated in the organogelator solution (3.0×10^{-5} M) for 1h.

2.2.6. Gelation tests of the organogelator

The organogelator was added to various organic solvents (1 wt%~10 wt%). If the compound was dissolved, the mixture was left still in ambient temperature for 1 h. Otherwise the compound remained precipitated in the solvent. If the mixture formed an organogel, it did not flow after turning it upside down (Vial-inversion method). And 1 mL of the same solvent was added and the mixture was heated and cooled down again repeatedly, until gelation did not occur.

2.2.7. Scanning electron microscopy

Field emission scanning electron microscopy (FE-SEM) images were obtained by using a JEOL JSM-6700F microscope. The organogels (0.75 wt%, 1 wt%, 3 wt% of organogelator in *n*-hexne and *n*-decane, respectively) were dried in vacuo for 3 days and the SWNTS/Gel composite (1 wt%, gelator : SWNTs = 100:1) was formed on the TEM grid.

2.2.8. Transmission electron microscopy

Transmission electron microscopy images were obtained by using a JEOL JEM-3000F microscope at 300 keV, a FEI Technai F20 microscope at 200 keV (for SWNTs/Gel composites) and a JEOL JEM-1010 microscope at 80 keV (for organogels). Gels (1 wt%, 0.75 wt%) were prepared in *n*-hexane and *n*-decane. The SWNTS/Gel composite (gelator : SWNTs = 100:1) was sonicated at 37 kHz for 1 h and dropped on a 300 mesh copper grid coated with carbon film. The samples were left in ambient temperature for 30 min and dried in vacuum oven overnight.

2.2.9. Thermal stability test of the gel and SWNTs/Gel composite

The gel and SWNTs/Gel composite samples were formed in vials and sealed with Teflon tape to prevent water penetration. The vials were immersed inversely in a water bath, and firmly fixed by a clamp to stand to observe gel-to-sol transition. The water bath was moderately stirred with a magnetic stir bar, and the temperature was increased by 1 ℃ at a time every 10 min from 30 ℃. The state of the gel was checked every 10 min and the temperature when broken gel dropped down to the bottom was recorded as the gel-to-sol transition temperature.

2.2.10. Rheological behavior analysis

Rheological properties were measured by Advanced rheometric expansion system (ARES, Rheometric Scientific) in oscillatory shear 1 % strain in the cone and plate geometry with a 25 mm plate. Frequency sweep tests from 0.1 to 500 rad/s were carried out at 25 ℃. Before performing measurement, organogelator solution (10 wt% in *n*-decane) and SWNTs/gel mixture (10 wt% in *n*-decane, gelator : SWNTs = 50:1, 25:1) were loaded on the plate. When the organogel and SWNTs/Gel composites were formed after 1h, rheological properties were measured.

2.2.11. Electrical conductivity measurement

The conductivities of the gel and SWNTs/Gel composite were measured by two probe technique (Alessi, probe station Rel-5500) at ambient temperature. The SWNTs/gelator solution (10 wt% in *n*-decane, gelator : SWNTs = 50:1) was used to make sample by a drop-casting method on the platinum plate (2.5 cm·2.5 cm), then the sample was dried at ambient temperature. Reference gel sample was made by a spin-coating method (thickness: 20 nm, measured by Gaertner Ellipsometer). After silver paste was added on the organogel film and naked platinum plate of same sample, resistances were measured, then conductivities were obtained using the equation related resistance and conductivity.

2.3. Synthesis

2.3.1. Synthesis of Methyl 3,4,5-tris(dodecyloxy)benzoate (1)

This compound was synthesized by the same procedure from previous literature.[47] Methyl 3,4,5- trihydroxybenzote (3.00 g, 16.3 mmol) and potassium carbonate (13.5 g, 97.8 mmol) were added in 50 mL DMF. The mixture was stirred at 80 ℃ for 2 h, and 20.3 g (81.5 mmol) of 1-bromododecane was added dropwise. The mixture was stirred at 80 ℃ overnight. After DMF was evaporated, the residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 39:1). The obtained powder was further purified by recrystallization in ethanol and white powder was obtained after vacuum filtration. Yield: 8.70 g, 77.6 %. ^{1}H NMR ($CDCl_3$) δ: 7.26 (2H, s), 4.03-3.99 (6H, t), 3.89 (3H, s), 1.83-1.79 (6H, m), 1.50-1.47 (6H, m), 1.26-1.22 (54H, m), 0.88-0.86 (9H, m).

2.3.2. Synthesis of 3,4,5-Tris(dodecyloxy)benzoic acid (2)

This compound was also synthesized by the same method from previous literature.[47] Methyl 3,4,5-tris(dodecyloxy)benzoate (1) (3.13 g, 4.54 mmol) and potassium hydroxide (1.28 g, 22.7 mmol) were added in 35 mL ethanol. The reaction mixture was heated at 80 ℃ for 3 h. Ethanol was removed by rotary evaporator. The residue was added dropwise in the distilled water (800 mL) with stirring. The aqueous solution was acidified with hydrochloric acid until the white solid was precipitated. The mixture was washed by distilled water and white powder was obtained. Yield: 2.91 g, 94.9 %. ^{1}H NMR ($CDCl_3$) δ: 7.30 (2H, s), 4.06-4.00 (6H, m), 1.84-1.72 (6H, m), 1.48-4.45 (6H, m), 1.38-1.27 (54H, m), 0.90-0.86 (9H, m)

2.3.3. Synthesis of *N*-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide (3)

This synthesis method was modified from previous literature.[48] Dry THF (20 mL) was added to a flame dried flask which was evacuated and refilled with nitrogen gas. 1.48 g (2.84 mmol) of (benzotriazol-1-yloxy) tripyrrolidinophosphonium hexafluorophosphate (PyBOP), 1.6 mL (23.3 mmol) of ethylene diamine, and 1.60 g (2.38 mmol) of 3,4,5-Tris (dodecyloxy) benzoic acid were added. The mixture was stirred overnight at 80℃. After THF was evaporated, the product was extracted with chloroform/distilled water. The extract was dried with magnesium sulfate. The pale white power was purified by column chromatography (silica gel, dichloromethane: methanol=19:1). Yield: 0.53 g, 31.2 %. ^{1}H NMR ($CDCl_3$) δ: 7.00 (2H, m), 6.55 (1H, s), 4.03-3.96 (6H, m), 3.52-3.48 (2H, t), 2.96-2.93 (2H, t), 1.83-1.71 (6H, m), 1.50-1.47 (6H, m). 1.40-1.26 (54H, m), 0.90-0.86 (9H, m)

2.3.4. Synthesis of 5-Bromo-3,4'-dihexyl-2,2'-bithiophene (4)

This compound was prepared by general synthesis method.[49] 3,4'-Dihexyl-2,2'-bithiophene (1.52 g, 4.54 mmol) were dissolved in DMF (5 mL). *N*-Bromosuccinimide (NBS) (0.81 g, 4.54 mmol) was added to the solution. The mixture was sonicated for 10 min. After DMF was evaporated, the product was extracted with diethyl ether/distilled water. The extract was dried with magnesium sulfate. The residue concentrated by rotary evaporator was purified by column chromatography (silica gel, *n*-hexane). The product was obtained as pale yellow liquid. Yield: 1.73 g, 92.1 %. ^{1}H NMR ($CDCl_3$) δ: 7.15-7.12 (1H, d), 6.90-6.87 (1H, d), 6.76 (1H, s), 2.72-2.67 (2H, t), 2.58-2.53 (2H, t), 1.65-1.55 (4H, m), 1.40-1.26 (12H, m), 0.89-0.87 (6H, m)

2.3.5. Synthesis of 3,4',4'',3'''-Tetrahexyl-2,2':5'5'':2'',2'''-quaterthiophene (5)

This synthesis method was modified to yamamoto coupling reaction.[50] 2,2’-

bipyridyl (1.03 g, 1.2 equiv.), 1,5- cyclooctadiene (0.82 mL, 1.2 equiv.) and bis(1,5-cyclooctadiene)nickel (0) (1.81 g, 1.2 equiv.) were added in dry DMF (30 mL). The mixture was stirred at 80 ℃ for 1 h. 4.56 g (11.0 mmol, 2 equiv.) of 5-bromo-3,4'-dihexyl-2,2'-bithiophene (4) was added and stirred overnight. The reaction mixture was cooled to room temperature and hydrochloric acid was dropped until color of the mixture turned green. After DMF was evaporated, the product was extracted with diethyl ether/distilled water. The extract was dried with magnesium sulfate. The residue concentrated by rotary evaporator was purified by column chromatography (silica gel, *n*-hexane). The product was obtained as yellow liquid. Yield: 1.91 g, 51.9 %. ^{1}H NMR ($CDCl_3$) δ: 7.16-7.15 (2H, d), 6.98 (2H, s) 6.93-6.92 (2H, d), 2.81-2.76 (4H, t) 2.58-2.53 (4H, t), 1.67-1.57 (8H, m), 1.40-1.30 (24H, m), 1.00-0.80 (12H, m)

2.3.6. Synthesis of 3,4',4'',3'''-Tetrahexyl-2,2':5'5'':2'',2'''-quaterthiophene-5,5'''-dicarbaldehyde (6)

Phosphorus (V) oxychloride (9.50 g, 62.0 mmol) and DMF (4.53 g, 62.0 mmol) were added in dichloromethane (20 mL) to prepare the Vilsmeier reaction.[51] The solution was stirred at 0 ℃ for 1 h. 2.01 g (3.1 mmol) of 3,4',4",3'"-tetrahexyl-2,2':5'5":2",2'"-quaterthiophene (5) was slowly added at 0 ℃. The mixture was refluxed overnight. 40 mL of 1 M sodium acetate solution was slowly added at 0 ℃ then extracted with dichloromethane/distilled water. The extract was dried with magnesium sulfate. The residue concentrated by rotary evaporator was purified by column chromatography (silica gel, dichloromethane/*n*-hexane=2:1). The product was obtained as yellow solid. Yield: 2.05 g, 94.1 %. ^{1}H NMR ($CDCl_3$) δ: 9.84 (2H, s), 7.59 (2H, s), 7.17 (2H, s), 2.85-2.80 (4H, m), 2.60-2.55 (4H, m)

2.3.7. Synthesis of organogelator (7)

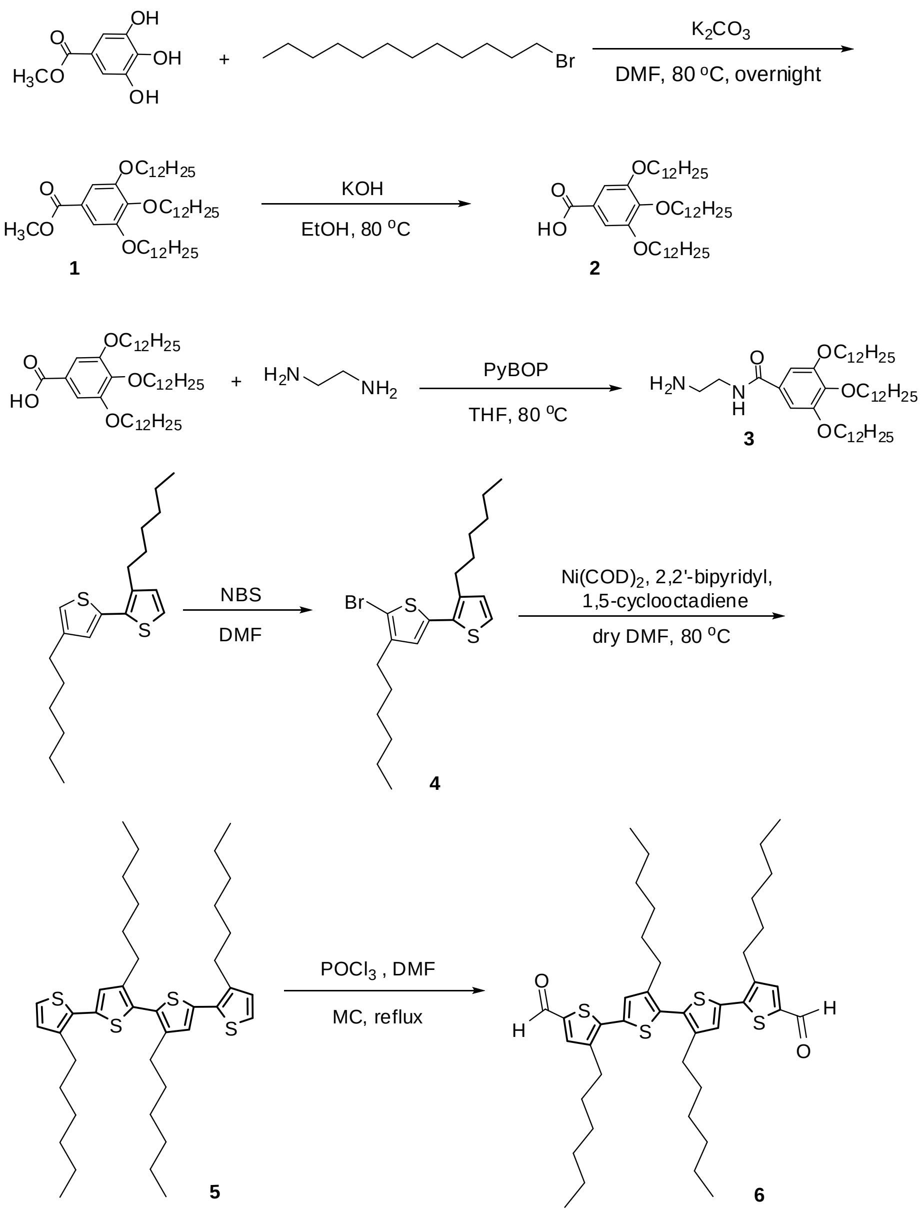
N-(2-aminoethyl)-3,4,5-tris (dodecyloxy) benzamide (3) (0.65 g, 0.90 mmol) and 3,4',4'',3'''-Tetrahexyl-2,2':5'5'':2'',2'''-quaterthiophene-5,5'''-dicarbaldehyde (6) (0.22 g, 0.30 mmol) were dissolved in chloroform (5 mL). Acetic acid (2 equiv.) was added, and then the solution was refluxed overnight. After evaporation of the solvent, the residue was washed with methanol. The crude product was recrystallized from dichloromethane/methanol and dried in vacuum oven. The orange solid was obtained. Yield: 0.63 g, 97.6 %. Anal. Calcd. (in wt%) for $C_{132}H_{222}N_4O_8S_4$: C, 74.73; H, 10.55; N, 2.64; S, 6.05. Found: C, 74.63; H, 10.53; N, 2.53; S, 6.05; ^{1}H NMR ($CDCl_3$) δ: 8.31 (2H, s), 7.13 (2H, s), 7.08 (2H, s), 6.93 (4H, s), 6.41 (2H, s), 3.99-3.94 (12H, m), 3.79 (8H, s), 2.80-2.74 (4H, t), 2.59-2.53 (4H, t), 1.78-1.74 (12H, t), 1.43-1.25 (108H, m), 0.89-0.86 (18H, m); ^{13}C NMR ($CDCl_3$) δ: 167.47, 156.03, 153.09, 143.03, 141.12, 139.59, 138.85, 135.64, 134.66, 133.97, 129.65, 129.02, 128.01, 105.59, 73.49, 69.26, 59.94, 40.63

31.93-31.65, 30.65-30.33, 29.71-28.99, 26.09, 22.68, 22.57, 14.09, 14.04; FT-IR (KBr pellet, cm^{-1}): 3275, 2923, 2853, 1630, 1582, 1542, 1501, 1471, 1431, 1389, 1342, 1237, 1123.

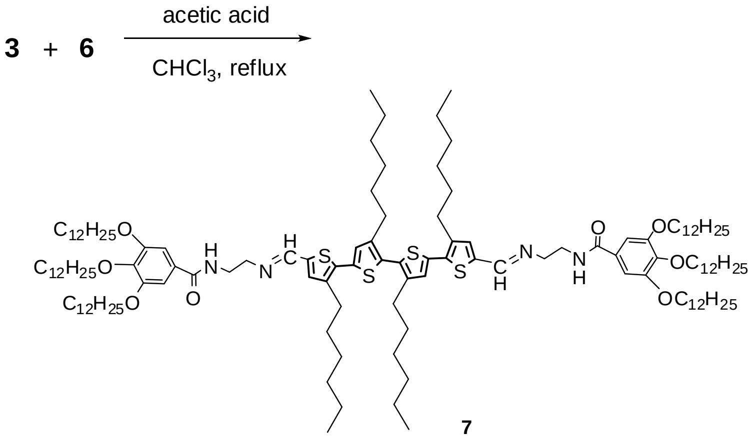
3. Results and Discussion

3.1. Synthesis of oligothiophene-based organogelator

Synthesis of the oligothiophene-based organogelator is outlined in Scheme 1. Three alkoxy tails were introduced to methyl 3,4,5-trihydroxybenzoate by S_N2 reaction with 1-bromododecane in DMF to yield compound 1. After hydrolysis, the trialkoxybenzoic acid went through amidation with ethylene diamine using PyBOP reagent. In order to synthesize thiophene core, 5-bromo-3,4'-dihexyl-2,2'-bithiophene was prepared by bromination with NBS. Quaterthiophene derivative was synthesized by Yamamoto-coupling reaction. Aldehyde groups were introduced to the both ends of the quaterthiophene by Vilsmeier reaction. The oligothiophene-based organogelator was prepared by imine condensation with benzamide and dialdehyde-quaterthiophene. Through condensation, the oligothiophene-based organogelator having two amide and imine groups was successfully prepared and confirmed by ^{1}H NMR (Figure 3), ^{13}C NMR spectrum (Figure 1. Appendix) and elemental analysis.



Scheme 1. Synthesis of the oligothiophene-based organogelator.



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Scheme 1. (Continued) Synthesis of the oligothiophene-based organogelator.

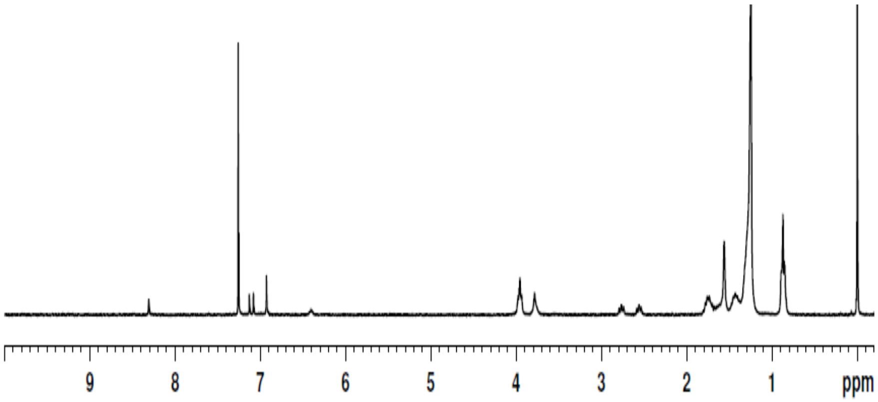

Figure 3. ^{1}H NMR spectrum of the oligothiophene-based organogelator (7) in $CDCl_3$.

3.2. Gel characterization

The organogelator could form an organogel in *n*-decane (Figure 4). Gelation only occurred in aliphatic solvents, because this organogelator had many long aliphatic chains. In addition, it was dissolved in non-polar and aprotic polar solvents. Table 1 shows the critical gelation concentration (CGC) of organogelator at room temperature and Table 2 shows the solubility properties of the organogelator in various solvents (5 wt%).

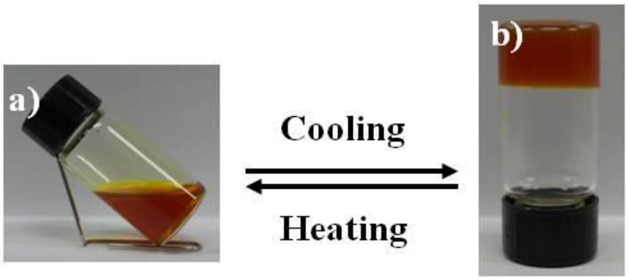

Figure 4. Photographs of sol state (a) and gel state (b) in *n*-decane (5 wt%).

Solvent	Critical gelation concentration (wt%)
n-Decane	3.0
n-Hexane	6.0

Table 1. Critical gelation concentrations (CGC) of the organogelator in aliphatic solvents.

Solvent	State	Solvent	State
Chloroform	sol	*N*,*N*-Dimethylformamide	precipitate
Methylene chloride	sol	Dimethylsulfoxide	precipitate
Toluene	sol	Methanol	precipitate
Tetrahydrofuran	sol	Water	precipitate

Table 2. Solubility properties of the organogelator in various solvents.

UV-Vis and photoluminescence experiments were performed in *n*-decane and tetrahydrofuran. In *n*-decane solution, the absorption maxima appeared at 257 nm and 372 nm. In case of tetrahydrofuran solution, the absorption maxima were blue-shifted to 253 nm and 369 nm, respectively, and new shoulder peak appeared at 291 nm (Figure 5-a). In PL spectra, the emission intensity in tetrahydrofuran decreased (Figure 5-b). These results suggested that tetrahydrofuran molecules interrupted hydrogen bonding between gelator molecules. It is known that tetrahydofuran molecules can participate in hydrogen bonding and have an affinity for alkyl group and conjugated molecule.[43] In conclusion, intermolecular hydrogen bonding played an important role in the self-assembly of this organogelator.

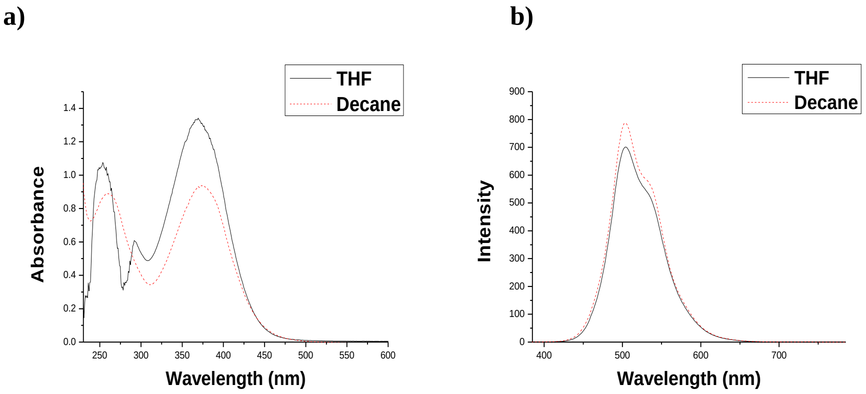

Figure 5. UV-Vis (a) and PL (b) spectra of gelator solutions in *n*-decane and tetrahydrofuran excited at 365 nm. The concentration of solutions was 3.0 × 10^{-5} M.

3.3. Dispersion and gelation properties of SWNTs/Gel composite

After SWNTs was incorporated into the gel, interactions between SWNTs and gelator molecules were inverstigated by FT-IR spectroscopy, UV-Vis spectroscopy and photoluminescence spectroscopy. The FT-IR spectra (Figure 6) showed absorbance at 3275 cm^{-1} (N-H stretching vibration), 1630 cm^{-1} (C=O stretching vibration, amide I), 1542 cm^{-1} (N-H bending vibration) and 1123 cm^{-1} (C-N stretching vibration) indicating the presence of secondary amide bond. The C=O stretching vibration peak slightly shifted to lower energy at 1626 cm^{-1} in the SWNTs/Gel composite, because carbonyl electrons delocalized to the π-electron cloud of SWNTs. The C-N stretching vibration absorption at 1123 cm^{-1} also shifted to higher wavenumber at 1133 cm^{-1}. The peaks at 2923 cm^{-1} and 2853 cm^{-1} were assigned to C-H stretching vibrations. The peak corresponding C-S stretching vibration of thiophene showed up at 847 cm^{-1}. The stretching vibration absorption of thiophene ring shifted from 1501 cm^{-1} to 1499 cm^{-1}, suggesting π-π interaction between oligothiophene core and SWNT.[36]

UV-Vis spectra (Figure 7-a) of the organogelator and SWNTs/gelator solution were compared. In conjugated molecules, the length of conjugation reflected the energy of the π-π* transition which appeared as the maximum absorption. The broad absorption peak of oligothiophene with absorption maximum at 372 nm indicated π-conjugation through oligothiophene core of organogelator molecule. The blue-shift of 6 nm observed at the absorption maximum (372 nm) and an additional shoulder peak (257 nm) in UV-Vis spectra. These changes were considered as an effect of the enhancement of π-π stacking between thiophene ring and surface of the CNT, compared to the dissolved gelator molecules in solvents.[37] Because adsorption could also occur from CH-π interaction,[38] the intensity of the absorption peaks were strongly enhanced after incorporating SWNTs. Furthermore, broad characteristic bands appeared around 650 and 900 nm. These wavelength ranges roughly matched to the band-to-band transitions of pure SWNTs. The CNTs used in measurement were comprised of two types (metallic and semiconducting), that was why the bands were broad.[39-40] PL spectra of the oligothiophene-based gelator (Figure 7-b) showed strong emission at 503 nm and 530 nm (shoulder band) when it was excited at 370 nm. After adding SWNTS, the peak intensity considerably decreased with a slight red-shift. Therefore, SWNTs were involved in energy transfer of excitons as an efficient fluorescence quencher.[41] These differences of absorption and emission spectrum might be induced by close packing which was provided by substituted hexyl groups of oligothiophene core.[42]

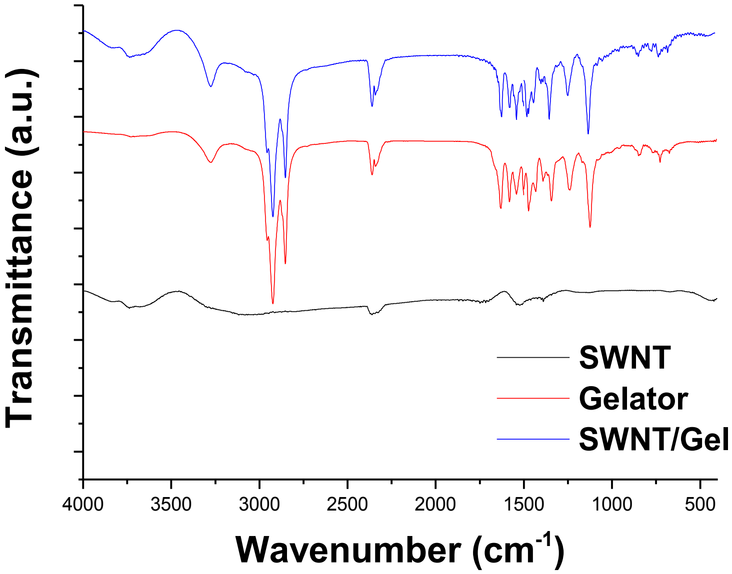

Figure 6. FT-IR spectra of the SWNTs, gelator, and SWNTs/Gel.

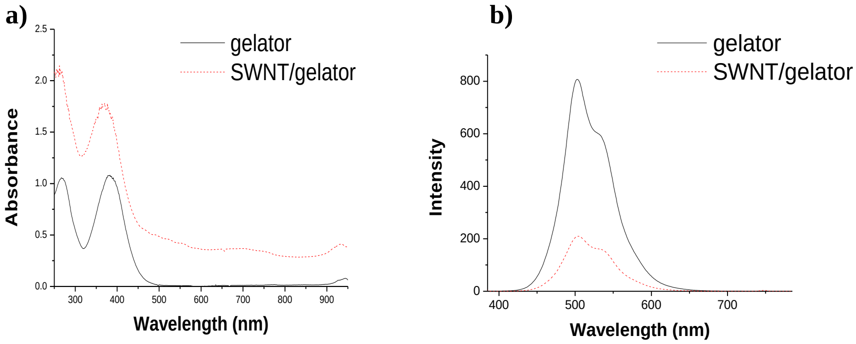

Figure 7. UV-Vis spectra (a) and PL spectra (b) of the gelator and SWNTs/gelator solution in *n*-decane excited at 370 nm. The solution concentration was 3.0×10^{-5} M and gelator: SWNTs= 50:1.

The dispersion of SWNTs in the SWNTs/Gel composite was investigated. Because of strong *van der Waals* interaction between themselves, even though SWNTs were sonicated for a long time, they could be easily aggregated in solvent. But interestingly, when the gelator and SWNTs were added in *n*-decane, a macroscopically homogeneous organogel composite was formed (Figure 8). The photographs of SWNTs in *n*-decane and the gel are shown in Figure 9. Aggregation of SWNTs was not observed in the composite. It suggested that organogelator encapsulated of SWNTs inside the gel fiber networks which prevented the aggregation.

The thermal stability of the SWNTs/Gel composites was investigated in order to confirm interaction between solvent molecule and this organogelator. Table 3 shows the gel-to-sol transition temperatures of several organogel systems, in various concentrations of SWNTs. The organogels formed in *n*-

decane showed small differences of thermal stability. As SWNTs were added more, gel-to-sol transition occurred at higher temperature. It indicated that thermal stability of SWNTs/Gel composite was enhanced by adding SWNTs. The gel of a higher gelator concentration was thermally more stable than that of a lower concentration, because excess organogelator molecules made a firm network structure.

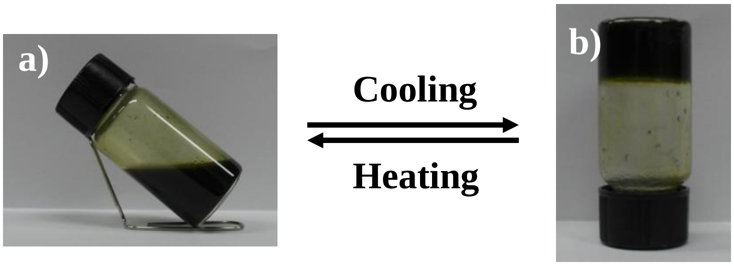

Figure 8. Photographs of sol state (a) and gel state (b) in *n*-decane (5 wt%, gelator: SWNTs=50:1).

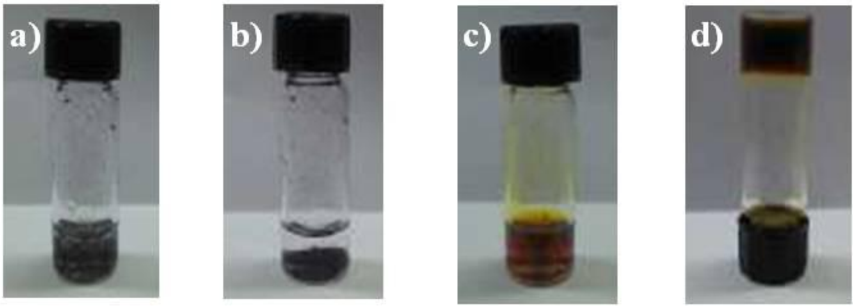

Figure 9. Photographs of SWNTs in *n*-decane after 1h of sonication (a), left for 10 min (b), SWNTs/Gel in solution state (c) and gel state (d) in *n*-decane (3 wt%, gelator: SWNTs=50:1).

gelator concentration gelator: SWNTs ratio	5 wt%	6 wt%
no SWNTs	44 ℃	45 ℃
100:1	44 ℃	45 ℃
50:1	45 ℃	46 ℃
25:1	46 ℃	46 ℃

Table 3. Gel-to-sol transition temperatures of the gels and SWNTs/Gel composites in *n*-decane.

3.4. Scanning electron microscopy images and transmission electron microscopy images of gel and SWNTs/Gel composite

Scanning electron microscopy images (Figure 10) of the dry gels obtained from different solvents showed slightly different morphologies. The dried gel in *n*-decane (Figure 10-a, b) was prepared as follows: the gel was first slowly dried at room temperature and placed in vacuum oven for 2 days. The SEM images of *n*-hexane gel (Figure 10-c, d) were obtained from dried gel. Gel fibers were observer from *n*-decane gel, while rod-like aggregates from the n-hexane gel with average diameter of 100-150 nm. Because *n*-hexane is volatile, it seemed that the gelator molecules could not have enough time to build gel fiber network structure in *n*-hexane. TEM images of *n*-decane and *n*-hexane gels showed similar morphologies (Figure 11). In these images, diameters of fibers were about 20-30 nm. Since the gel samples for SEM and TEM analysis were prepared in different concentrations, the diameters of gel fiber were different.

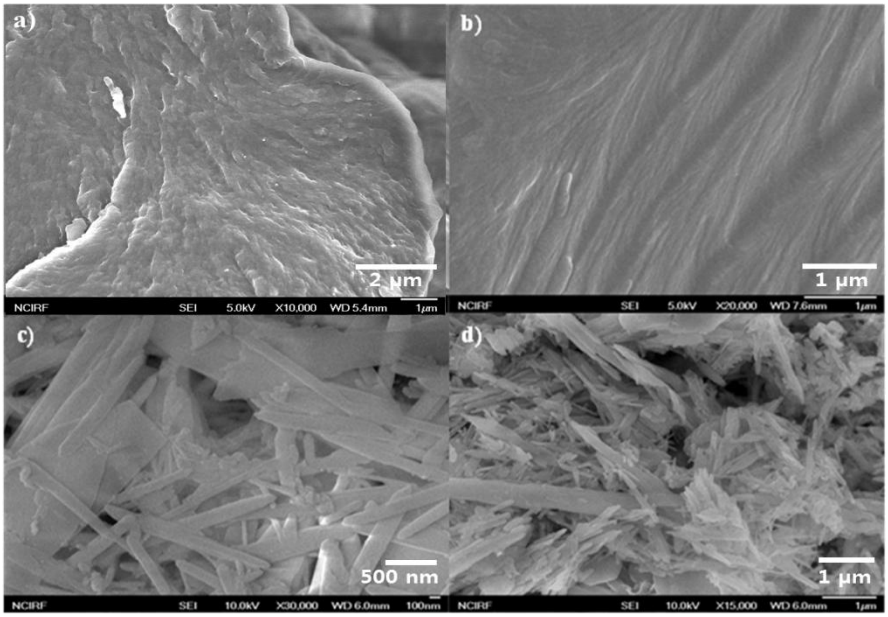

Figure 10. SEM images of organogels prepared in *n*-decane (3 wt%) (a) and (b), in *n*-hexane (1 wt%) (c) and (d).

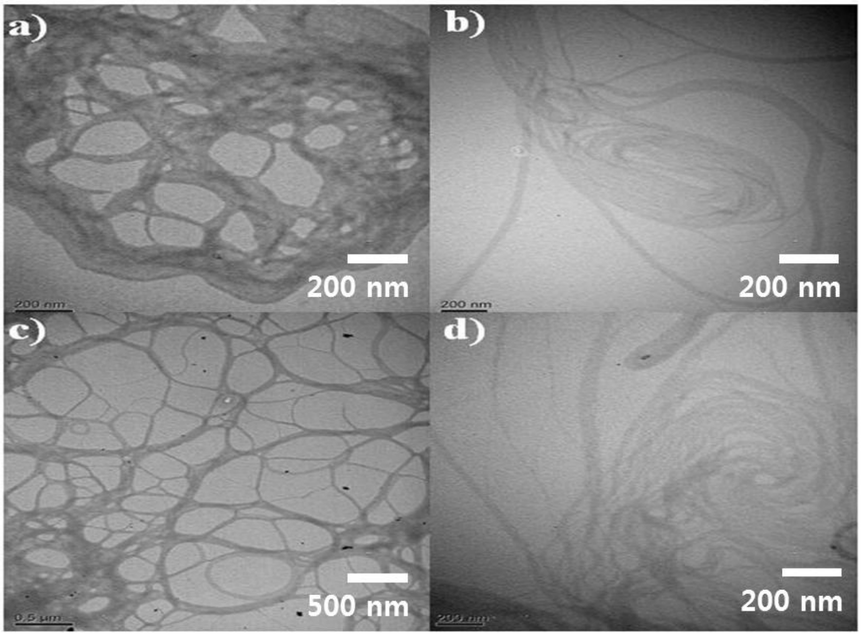

Figure 11. TEM images of organogels prepared in *n*-decane (0.2 wt%) (a) and (b), in *n*-hexane (0.5 wt%) (c) and (d).

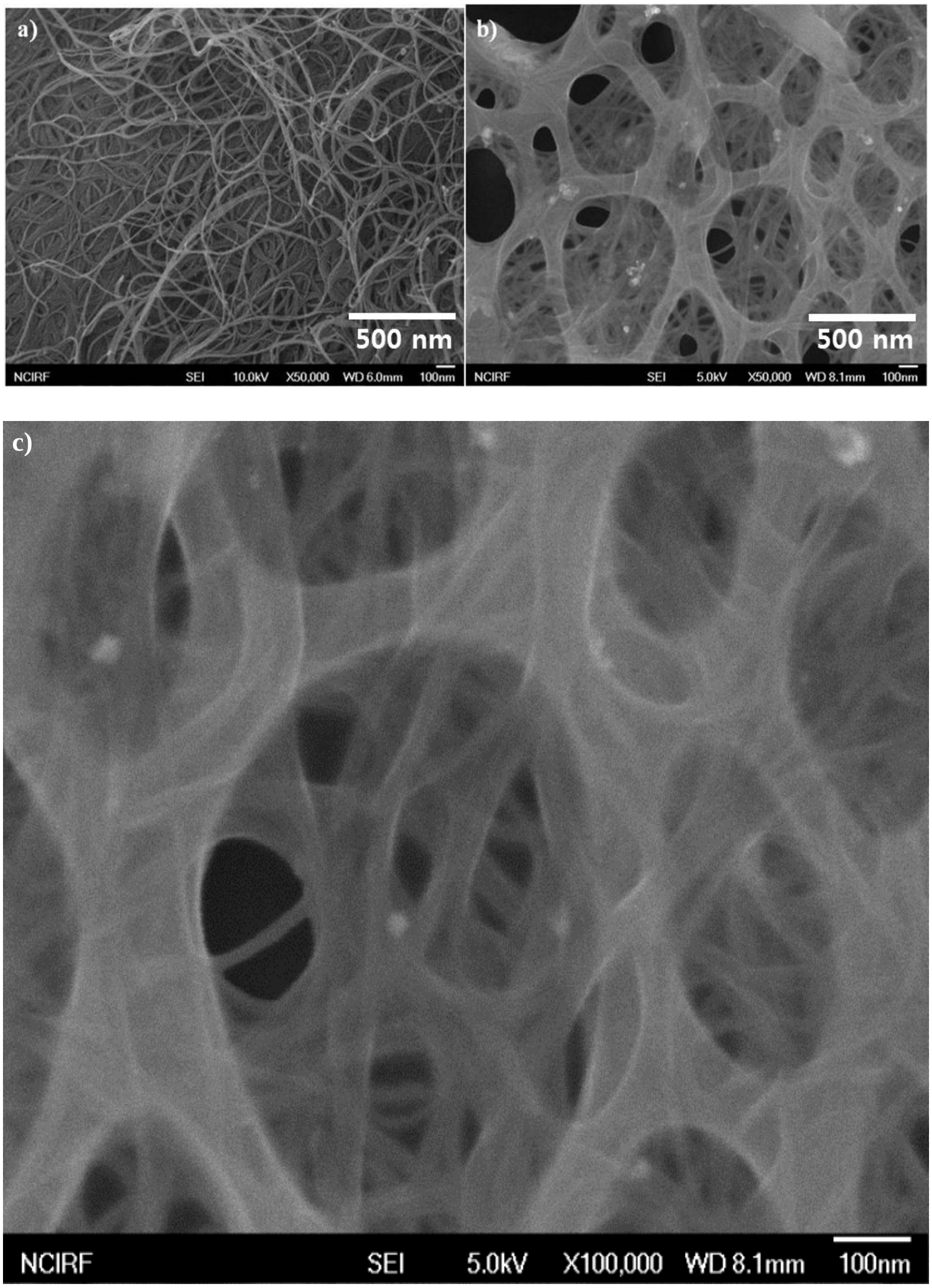

Figure 12. SEM images of aggregated pristine SWNTs (a), SWNTs/Gel composite (b) and (c) prepared in *n*-hexane on the TEM grid with carbon film (1 wt%, gelator: SWNTs=100:1).

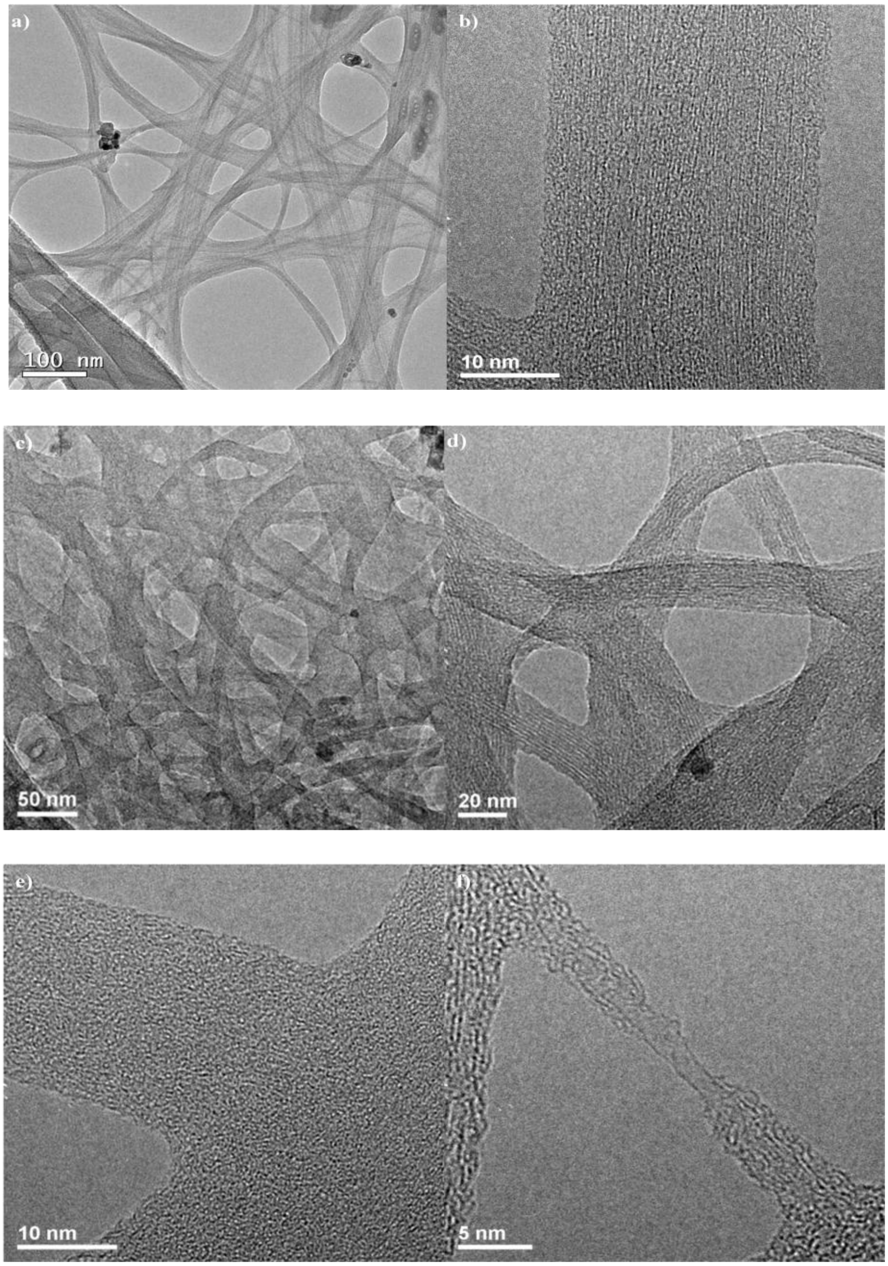

Figure 13. TEM images of SWNTs/Gel composite prepared in *n*-decane (0.5 wt%, gelator: SWNTs=25:1) (a) and (b), in *n*-hexane (1 wt%, gelator: SWNTs=100:1) (c), (d), (e) and (f).

Figure 12 shows the morphologies of SWNTs/organogel composite. In the SEM images, pristine SWNTs without any treatment existed as entangled bundles (Figure 12-a). However in the SWNTs/Gel composite, SWNTs were dispersed (Figure 12-b, c). For accurate observation of the morphology, transmission electron microscopy (TEM) was used. The TEM images of SWNTs/organogel show that small SWNTs bundles were incorporated into the gel firbers (Figure 13.) THE surfaces of SWNTs were coated with gelator with the gelator molecules owing to the π-π interaction between oligothiophenes of gelator and SWNTs.

3.5. Rheological properties of gel and SWNTs/Gel composite

Rheological studies were performed in order to find out the effect of the SWNTs incorporation into the organogel. The storage (G') and loss moduli (G") were obtained as a function of angular frequency range (0.1-500 rad/s) at a fixed strain of 0.1% through oscillatory frequency sweep test. Figure 14 shows the variation of G' and G" of the SWNTs/Gel composites as compared to native *n*-decane gel. If G' is larger than G" in the low frequency region, the system is considered as a gel.[44] The G' values of organogel and SWNTs/Gel composites were larger than their G" values. Dynamic mechanical properties of organogel and SWNTs/Gel composites were related with the concentration of SWNTs. At a ratio of gelator : SWNTs = 50:1, the composite showed better elastic property and at a ratio of gelator : SWNTs = 25:1, both storage moduli increased 5 times compared to the native organogel (Table 4). It indicated that a more elastic solid-like material was formed by incorporating of the SWNTs into the native gel, and the composite had greater resistance to flow behavior than the native organogel. It is well known that this phenomenon is attributed to the π-π stacking interaction between CNTs and π-conjugated moieties.[45] Aliphatic chains of oligothiophene core could also interact with the SWNTs. These modulus values were comparable with those of other CNT composites previously reported.[42]

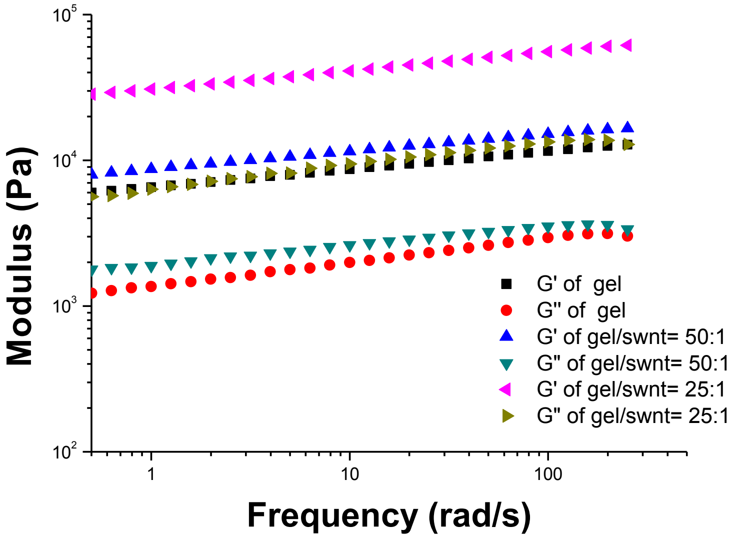

Figure 14. Dynamic mechanical property versus angular frequency plots of gel (10 wt%) and SWNTs/Gel composites (gelator: SWNTs=50:1, 25:1) in *n*-decane.

Sample	Storage modulus (Pa)	Loss modulus (Pa)
Native gel	8674	1986
SWNTs/Gel (1:50)	11542	2622
SWNTs/Gel (1:25)	41031	9454

Table 4. Dynamic mechanical properties of gel (10 wt%) and SWNTs/Gel composites (gelator: SWNTs= 50:1, 25:1) at 10 rad/s.

3.6. Electrical properties of gel and SWNTs/Gel composite

In order to measure electrical property of SWNTs/Gel composite, the films were prepared by solvent drop-casting method. At first, a SWNTs/gel mixture in *n*-decane (10 wt%, gelator : SWNTs = 50:1) was dropped on the platinum plate. After drying, silver paste was put on the two points of the sample. Upon the voltage was applied on the film via two probes, the amount of current generated was measured. The I-V curve followed Ohm's law in the low voltage range and the corresponding resistance (R) was calculated from the I–V curve (Figure 15). The conductivity of the SWNTs/Gel composite film (5.33×10^{-12} S/m) was 100-fold larger than the conductivity of the reference gel film (6.63×10^{-14} S/m). The SWNTs were probably well-wrapped by the oligothiophene-based organogelator through π−π and CH−π interaction and which could cause a significant hindrance in charge transport, thereby lowering the conductivity from that of pure SWNTs. The SWNTs were probably well-wrapped by the oligothiophene-based organogelator molecules through π−π and CH−π interaction, which could cause a significant hindrance in charge transport and lowering the conductivity.

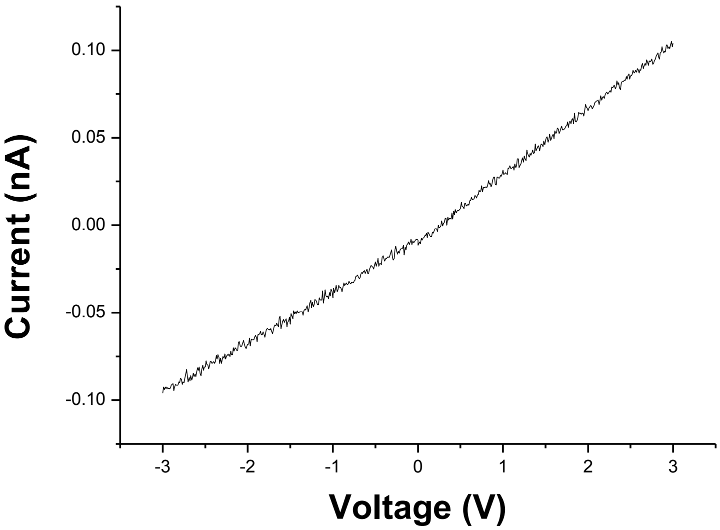

Figure 15. Electrical conductivity (I-V curve) of SWNTs/Gel composite.

4. Conclusion

We synthesized a new oligothiophene-based organogelator having two amide and imine groups. Organogels were formed in aliphatic solvents, *n*-decane and *n*-hexane. SWNTs/Gel composites were prepared through incorporation of SWNTs into the organogel. We performed UV-Vis, PL and FT-IR spectroscopy and discovered that the organogelator molecules were self-assembled by hydrogen bonding and π-π stacking interaction. The dispersion of SWNTs macroscopically looked like homogeneous, SEM and TEM images showed that this organogelator formed 1-D fiber network structure and SWNTs were incorporated into the gel fiber. In rheological study, gel and SWNTs/Gel composites showed enhanced storage moduli by incorporation of SWNTs. We measured the conductivity of composite, but the value was very low due to the lack of extensive π-conjugated length. SWNTs were possibly well-wrapped by the near-insulating organogelator through π−π and CH−π interaction. The organogel composite could have potential applications in organic electric fields, if electrical property of SWNTs/Gel composite would be improved.

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APPENDIX

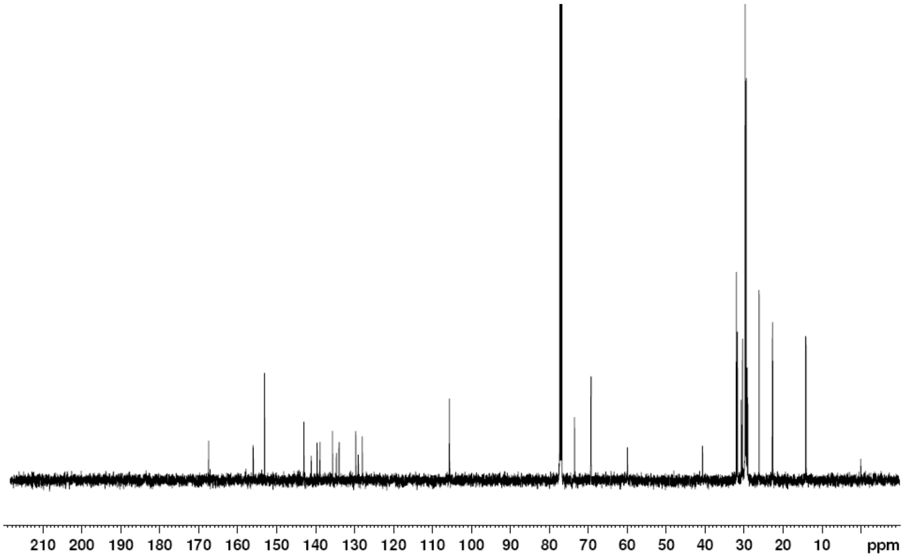

Figure 1. ^{13}C NMR spectra of the oligothiophene-based organogelator.

국문 요약

본 연구에서는 올리고사이오펜 기반의 새로운 유기젤레이터를 합성하고 이를 이용하여 유기젤과 탄소 나노튜브/젤 복합체를 제조하였다. 탄소 나노튜브는 큰 종횡 비와 뛰어난 전기적, 화학적, 기계적 성질을 가지고 있어서 다양한 분야에서 각광받고 있는 재료이다. 그러나 탄소 나노튜브는 튜브간의 강한 반데르 발스 힘에 의해서 쉽게 응집된다. 본 연구에서는 양끝에 알데히드그룹을 갖는 올리고사이오펜과 긴 알킬 체인을 갖는 벤자아미드 유도체를 이민 축합반응 시켜 젤레이터를 합성하고, 이로부터 제조한 유기젤에 탄소나노튜브를 분산시켰다. 탄소 나노튜브/젤 복합체는 젤레이터 용액에 단일벽 탄소 나노튜브를 섞어서 제조하였다. 올리고사이오펜과 탄소 나노튜브간의 강한 인력에 의해서 탄소나노튜브가 유기젤에 잘 분산되는 것을 SEM과 TEM 분석으로 확인하였다. 자외선-가시광선. 형광, 적외선 분광법를 이용하여 젤레이터의 자기조립과 복합체 내의 인력을 조사하였다. 유변학적 분석 및 전도도 측정을 통해서 탄소 나노튜브/젤 복합체가 유기젤보다 향상된 동역학적 특성과 전기전도도를 갖는 것을 확인하였다.

주요어: 유기 젤, 탄소 나노튜브, 올리고사이오펜, 복합재료, 분산, 자기조립

Student Number: 2011-20640