Polymer 50 (2009) 1395–1402

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Amphiphilic polythiophene for the formation of gold nanowire networks

Young-Sik Yoon, Hae-Sung Sohn, Jong-Chan Lee*

Department of Chemical and Biological Engineering, Seoul National University, 599 Gwanangno, Gwanak-Gu, Seoul 151-744, Republic of Korea

ARTICLE INFO

Article history:
Received 9 September 2008
Received in revised form
17 January 2009
Accepted 23 January 2009
Available online 29 January 2009

Keywords:
Polythiophene
Gold
Conducting polymer

ABSTRACT

Polythiophene containing amphiphilic decyl-tri(oxyethylene) side group was synthesized. Gold nanowire networks having almost uniform wire diameters could be prepared when the amphiphilic polythiophene was mixed with hydrogen tetrachloroaurate ($HAuCl_4$) in THF followed by the addition of aqueous sodium borohydride solution. The size of nanowire networks and the diameter of the component wires could be controlled by changing the polymer concentration and the gold salt to polymer ratios. When polythiophene derivatives having hydrophobic or hydrophilic side groups were used instead of the amphiphilic polythiophene, disconnected poor networks and coagulated nanoparticle chunks, respectively, were obtained, although the same reduction process was applied.

1. Introduction

Conducting polymers have been widely studied over the past few decades due to their unique semiconducting and optoelectronic properties [1–5]. Recently, inorganic nanomaterials such as nanoparticles and one-dimensional nanostructures including carbon nanotubes have been incorporated into conducting polymers to produce conducting nanocomposites [6–14]. The addition of nanomaterials to conducting polymer matrices can improve or tune the electrical and mechanical properties of nanocomposites by adjusting the composition and the dispersions of the nanomaterials [9–11]. Since nanomaterials have interesting optical, electrochemical, and photoelectrochemical properties, they can be used in important applications such as electrochromic devices, microwave absorbers, photovoltaic cells, sensors, etc [15–24]. Two-dimensional nanowire networks have also attracted much attention for their potential applications in microelectronics, nanocatalysis, nanofillers in composites, and as interconnections for nanoscale electronic devices. Procedures for the synthesis of the nanowire networks such as template-direct methods using polymeric nanostructures [25,26], organic surfactants [27–30], a hard template method [31], and a templateless method [32] based on a coalescence process by agitation of nanoparticles in biphasic mixtures have been developed.

Herein we report the synthesis of a polythiophene having decyl-tri(oxyethylene) side chain groups. Having side groups with amphiphilic character composed of hydrophilic tri(oxyethylene) and hydrophobic decyl groups, it was expected that this conducting polymer could be used as a template for nanomaterials formation. Previously, amphiphilic polymer brushes used as template for the formation of one-dimensional metal and semiconductor nanostructures because metallic ionic precursors are preferentially located in the nano-sized hydrophilic region, and the subsequent reduction of the precursors produces nanomaterials with different sized nanorods and nanowires [25,33]. This time we could prepare gold nanowire networks having uniform wire diameters when the polymer was mixed with gold salt followed by a chemical reduction process, and the amphiphilic character of the polymer was found to be crucial for the formation of these nanowire networks. The synthesis and characterization of the amphiphilic polythiophene, the preparation of the nanowire networks using the polythiophene, and the effect of the side group character of the polythiophene templates on the formation of nanomaterials are described here.

2. Experimental methods

N-Methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), ethanol, and methanol were dried over molecular sieves (4 Å). Tetrahydrofuran (THF) was dried over CaH_2 for 24 h under nitrogen atmosphere and distilled. 1-Bromodecane, triethylene glycol, 3-bromothiophene, [1,3-bis(diphenylphosphino)propane]-dichloronickel(II) ($Ni(dppp)Cl_2$), *N*-bromosuccinimide (NBS), sodium hydride (NaH), copper bromide (CuBr), sodium (Na), and poly(3-decylthiophene) were purchased from Aldrich and they were used without further purification. All other reagents and solvents were used as received.

---

* Corresponding author. Tel.: +82 2 880 7070; fax: +82 2 888 1604.
E-mail address: jongchan@snu.ac.kr (J.-C. Lee).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.01.051

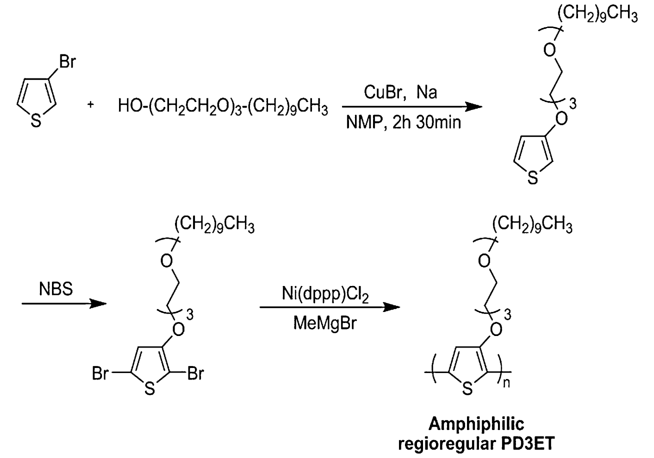

Fig. 1. Synthetic route of novel regioregular PD3ET with amphiphilic side groups.

2.1. *2-[2-(2-Decyloxyethoxy)ethoxy]ethanol*

1-Bromodecane (13.4 g, 60.4 mmol) was added dropwise at 0 °C to a stirred mixture of triethylene glycol (9.07 g, 60.4 mmol) and sodium hydride (1.45 g, 60.4 mmol) in 200 mL of dimethylacetamide (DMAc). After 3 h, the reaction was quenched by the dropwise addition of distilled water and the reaction mixture extracted with methylene chloride and 0.5 N aqueous HCl (1/1, vol/vol), dried over anhydrous magnesium sulfate, and concentrated, producing an oily liquid. The crude product was purified by column chromatography using SiO_2 as the stationary phase and ethyl acetate/hexane (1/2, vol/vol) as the eluent to produce 6.06 g (34% yield) of 2-[2-(2-decyloxyethoxy)ethoxy]ethanol. ^{1}H NMR ($CDCl_3$, δ/ppm): $\delta = 0.88$ (t, –CH_2CH_3, 3H), 1.20–1.40 (m, –$CH_2(CH_2)_7CH_3$, 14H), 1.58 (m, –$OCH_2CH_2(CH_2)_7CH_3$, 2H), 2.57 (br, –CH_2CH_2OH, 1H), 3.45 (t, –$OCH_2CH_2(CH_2)_7CH_3$, 2H), 3.55–3.79 (m, –$(OCH_2CH_2)_2OCH_2(CH_2)_8CH_3$, 8H) 3.53–3.78 (m, –$(CH_2CH_2O)_3$–, 12H). ^{13}C NMR ($CDCl_3$, δ/ppm): 13.92 (–CH_3), 22.49 (–CH_2CH_3), 25.90–29.43 (–$CH_2(CH_2)_6CH_2CH_2CH_3$), 31.73 (–$CH_2CH_2CH_3$), 61.32 (–CH_2OH), 69.86 (–CH_2CH_2OH), 70.17–71.34 (–$(OCH_2CH_2)_2OCH_2CH_2OH$), 72.49 (–$OCH_2(CH_2)_8CH_3$).

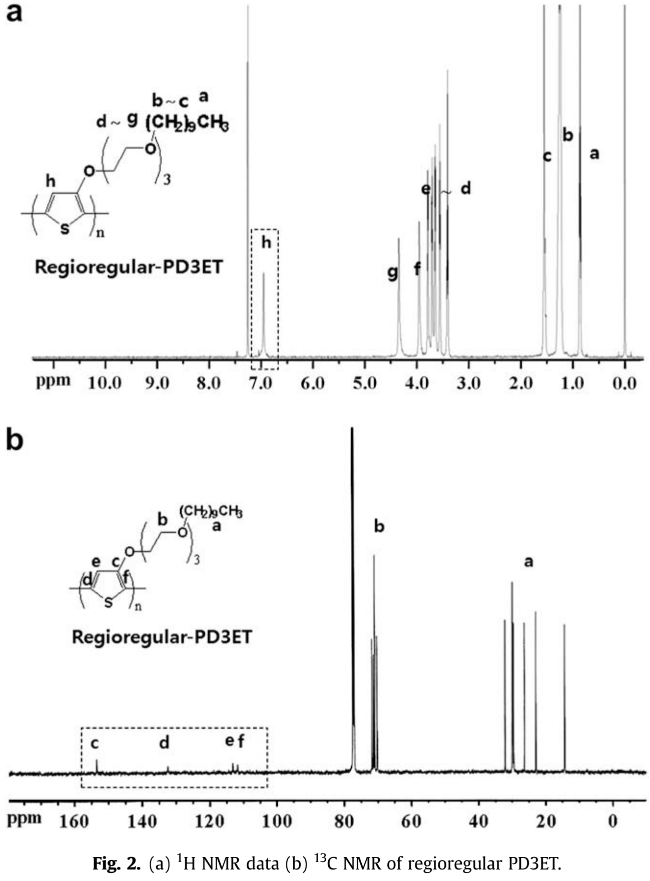

Fig. 2. (a) ^{1}H NMR data (b) ^{13}C NMR of regioregular PD3ET.

2.2. *3-{2-[2-(2-Decyloxyethoxy)ethoxy]ethoxy}thiophene (D3ET)*

2-[2-(2-Decyloxyethoxy)ethoxy]ethanol (14.9 g, 51.4 mmol) was added to a mixture of sodium (1.42 g, 61.7 mmol) and methanol (30.0 mL). After stirring at room temperature for 2 h and 30 min, the solvent was evaporated and a solid residue was obtained. Then, 3-bromothiophene (2.88 g, 17.7 mmol), CuBr (2.95 g, 20.6 mmol), and NMP (30.0 mL) were added to the reaction flask and the reaction mixture magnetically stirred at 140 °C for 2 h and 30 min. The solution was then allowed to cool to room temperature and the NMP was removed at 150 °C by rotary evaporation. After extraction of the concentrated mixture with 0.5 N aqueous HCl and methylene chloride (1/1, vol/vol) and drying over anhydrous magnesium sulfate, the solution was concentrated by using a rotary evaporator to produce an oily liquid. The crude product was purified by column chromatography using SiO_2 as the stationary phase and a mixture of ethyl acetate/hexane (1/4, vol/vol) as the eluent. The fraction with an R_f of 0.25 was collected and concentrated as above to yield 2.63 g (40% yield) of a light yellow oil. ^{1}H NMR ($CDCl_3$, δ/ppm): $\delta = 0.88$ (t, –CH_2CH_3, 3H), 1.26 (m, –$CH_2(CH_2)_7CH_3$, 14H), 1.57 (m, –$OCH_2CH_2(CH_2)_7C_3$, 2H), 3.43 (t, –$OCH_2CH_2(CH_2)_7CH_3$, 2H), 3.55–3.79 (m, –$(OCH_2CH_2)_2OCH_2(CH_2)_8CH_3$, 8H) 3.85 (m, –$CH_2CH_2O$–thiophene ring, 2H), 4.11 (m, –CH_2CH_2O–thiophene ring, 2H), 6.26 (dd, H-2, 1H), 6.78 (dd, H-4, 1H), 7.26 (dd, H-5, 1H). ^{13}C NMR ($CDCl_3$, δ/ppm): 14.12 (–CH_3), 22.71 (–CH_2CH_3), 26.12–29.64 (–$CH_2(CH_2)_6CH_2CH_2CH_3$), 31.93 (–$CH_2CH_2CH_3$), 69.57 (–$OCH_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3$), 69.69 (–$OCH_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3$), 70.06–70.81(–$OCH_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3$), 71.55 (–$OCH_2(CH_2)_8CH_3$), 97.48 (C-2), 119.59 (C-4), 124.61 (C-5), 157.58 (C-3).

2.3. *2,5-Dibromo-3-{2-[2-(2-decyloxyethoxy)ethoxy]-ethoxy}thiophene*

3-{2-[2-(2-Decyloxyethoxy)ethoxy]ethoxy}thiophene (2.42 g, 6.51 mmol) was dissolved in chloroform and acetic acid and *N*-bromosuccinimide (2.54 g, 14.3 mmol) were added to the solution at

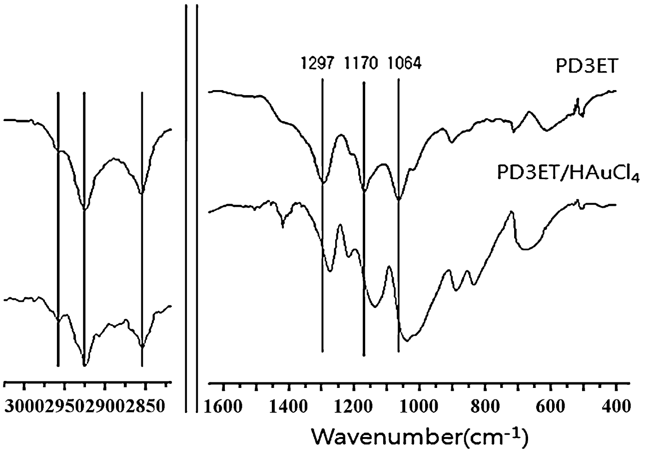

Fig. 3. FT-IR spectrum of PD3ET and PD3ET/$HAuCl_4$ complex.

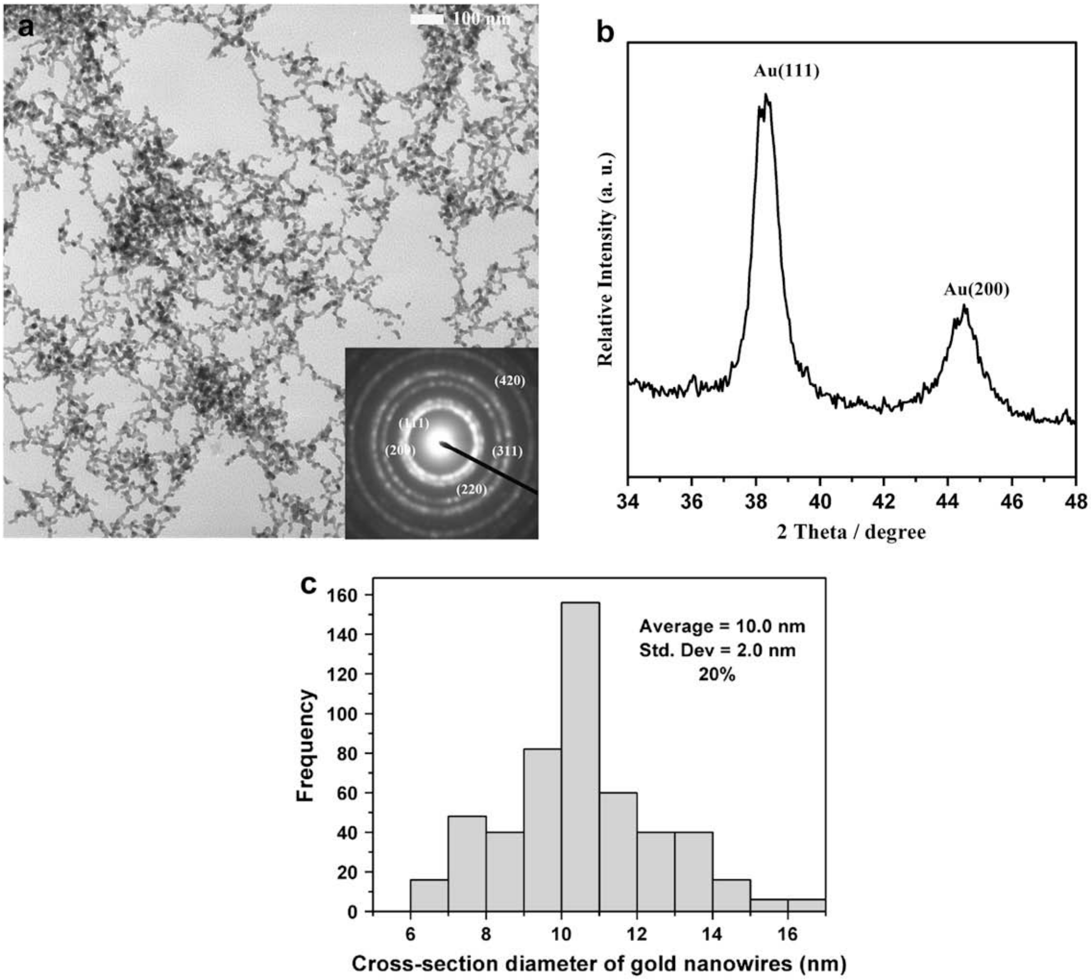

Fig. 4. (a) TEM image of 2D gold nanowire networks obtained using THF solution containing 4 mM $HAuCl_4$, 10 mM PD3ET, and 200 mM $NaBH_4$ aqueous solution. (b) X-ray diffraction spectrum of 2D gold nanowire networks. (c) Plot of frequency versus cross-sectional diameter for 510 randomly selected sections of the gold nanowire network as shown in Fig. 4(a).

0 °C, and the mixture was stirred for 6 h. The reaction mixture was then extracted with distilled water and chloroform (1/1, vol/vol), crude product was purified by column chromatography using ethyl acetate/hexane (1/5, vol/vol). The product was isolated as 1.20 g of a yellow oil (yield: 35%). ^{1}H NMR ($CDCl_3$, δ/ppm): $\delta = 0.88$ (t, $-\mathrm{CH_2}\text{-}\mathrm{C}H_3$, 3H), 1.26 (m, $-\mathrm{CH_2(C}H_2)_7\mathrm{CH_3}$, 14H), 1.57 (m, $-\mathrm{OCH_2C}H_2\mathrm{(CH_2)_7C_3}$, 2H), 3.47 (t, $-\mathrm{O}CH_2\mathrm{CH_2(CH_2)_7CH_3}$, 2H), 3.58–3.78 (m, $-(\mathrm{O}CH_2\text{-}CH_2)_2\mathrm{OCH_2(CH_2)_8CH_3}$, 8H) 3.86 (m, $-CH_2\mathrm{CH_2O}$–thiophene ring, 2H), 4.14 (m, $-\mathrm{CH_2}CH_2\mathrm{O}$–thiophene ring, 2H), 6.87 (s, thiophene ring protons, 1H). ^{13}C NMR ($CDCl_3$, δ/ppm): 14.12 ($-CH_3$), 22.67 ($-C\mathrm{H_2CH_3}$), 26.01–29.64 ($-\mathrm{CH_2(}C\mathrm{H_2)_6CH_2CH_2CH_3}$), 31.89 ($-C\mathrm{H_2CH_2CH_3}$), 69.81 ($-\mathrm{O}C\mathrm{H_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3}$), 70.07 ($-\mathrm{OCH_2}C\mathrm{H_2(OCH_2CH_2)_2O(CH_2)_9CH_3}$), 70.69–71.52 ($-\mathrm{OCH_2CH_2(O}C\mathrm{H_2}C\mathrm{H_2)_2O(CH_2)_9CH_3}$), 72.03 ($-\mathrm{O}C\mathrm{H_2(CH_2)_8CH_3}$), 91.31 (C-2), 109.54 (C-5), 121.49 (C-4), 153.74 (C-3).

2.4. *Regioregular poly(3-{2-[2-(2-decyloxyethoxy)ethoxy]ethoxy}-thiophene) (PD3ET)*

2,5-Dibromo-3-{2-[2-(2-decyloxyethoxy)ethoxy]ethoxy}thiophene (1.20 g, 2.26 mmol) was dissolved in THF solvent (20.0 mL) and 3.0 M methylmagnesium bromide/diethylether solution (equivalent to 0.75 g, 2.26 mmol of the bromide) was added. After 2 h of reflux with stirring, Ni(dppp)Cl_2 catalyst (0.12 g, 0.0226 mmol) was added to the mixture and refluxed for an additional 2 h. When polymerization was completed, the polymer was precipitated by adding the solution into methanol, and the resulting black precipitate was washed by Soxhlet extraction using methanol and hexane for 24 h, respectively, to produce 0.50 g (59% yield) of black solid. ^{1}H NMR ($CDCl_3$, δ/ppm): $\delta = 0.86$ (t, $-\mathrm{CH_2C}H_3$, 3H), 1.23 (m, $-\mathrm{CH_2(C}H_2)_7\mathrm{CH_3}$,14H), 1.53 (m, $-\mathrm{OCH_2C}H_2\mathrm{(CH_2)_7C_3}$, 2H), 3.41 (t, $-\mathrm{O}CH_2\mathrm{CH_2(CH_2)_7CH_3}$, 2H), 3.55–3.80 (m, $-(\mathrm{O}CH_2CH_2)_2\mathrm{OCH_2(CH_2)_8CH_3}$, 8H), 3.95 (t, $-CH_2\mathrm{CH_2O}$–thiophene ring, 2H), 4.35 (t, $-\mathrm{CH_2}CH_2\mathrm{O}$–thiophene ring, 2H), 6.96 (s, thiophene ring protons, 1H). ^{13}C NMR ($CDCl_3$, δ/ppm): 14.31 ($-CH_3$), 22.89 ($-C\mathrm{H_2CH_3}$), 26.32–29.88 ($-\mathrm{CH_2(}C\mathrm{H_2)_6CH_2CH_2CH_3}$), 32.12 ($-C\mathrm{H_2CH_2CH_3}$), 70.16 ($-\mathrm{O}C\mathrm{H_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3}$), 70.25 ($-\mathrm{OCH_2}C\mathrm{H_2(OCH_2\text{-}CH_2)_2O(CH_2)_9CH_3}$), 70.95–71.32 ($-\mathrm{OCH_2CH_2(O}C\mathrm{H_2}C\mathrm{H_2)_2O(CH_2)_9CH_3}$), 71.77 ($-\mathrm{O}C\mathrm{H_2(CH_2)_8CH_3}$), 111.68 (C-2), 113.15 (C-4), 132.49 (C-5), 153.42 (C-3).

2.5. *Regiorandom poly(3-{2-[2-(2-decyloxyethoxy)ethoxy]ethoxy}-thiophene) (regiorandom PD3ET)*

A solution of 3-{2-[2-(2-decyloxyethoxy)ethoxy]ethoxy}-thiophene (D3ET) (0.37 g, 0.99 mmol) in dry chloroform (50.0 mL) was added to a solution of anhydrous $FeCl_3$ (0.67 g, 0.40 mmol) in dry chloroform. The reaction mixture was stirred at 0 °C for 24 h, the

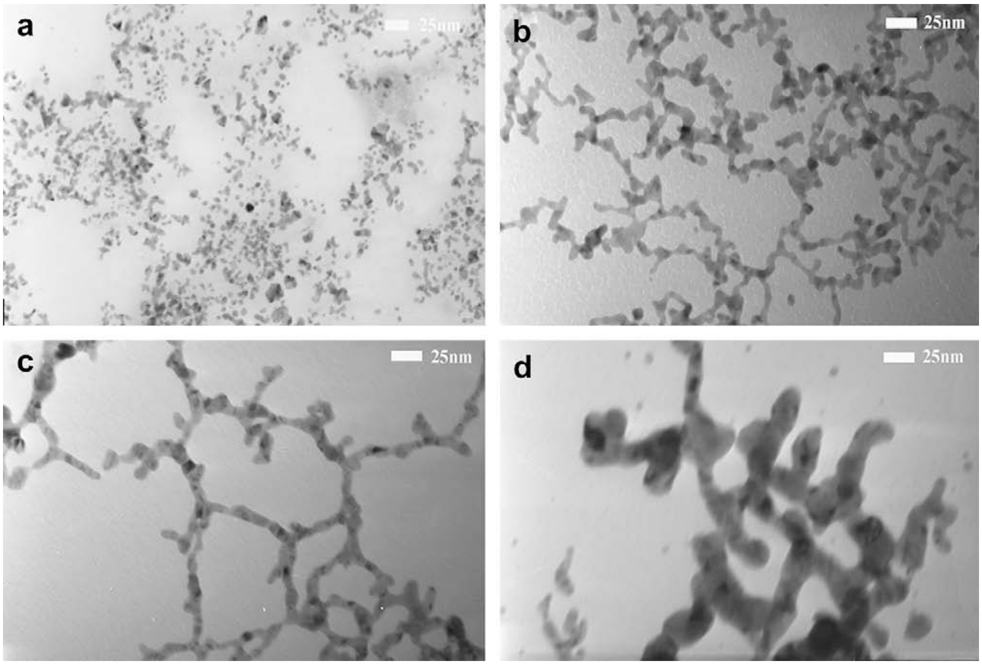

Fig. 5. TEM images of gold nanomaterials obtained using 200 mM $NaBH_4$ aqueous solution and (a) 0.04 mM $HAuCl_4$, 10 mM PD3ET; (b) 0.4 mM $HAuCl_4$, 10 mM PD3ET; (c) 4 mM $HAuCl_4$, 10 mM PD3ET; (d) 8 mM $HAuCl_4$, 10 mM PD3ET in THF solution.

crude product precipitated in methanol, the polymer was purified by extraction with methanol using a Soxhlet apparatus for 24 h, and the result was 0.16 g of product (43% yield). ^1H NMR ($CDCl_3$): $\delta = 0.86$ ppm (t, $-CH_2CH_3$, 3H), 1.24 ppm (m, $-CH_2(CH_2)_7CH_3$,14H), 1.55 ppm (m, $-OCH_2CH_2(CH_2)_7C_3$, 2H), 3.41 ppm (t, $-OCH_2CH_2(CH_2)_7CH_3$, 2H), 3.57–3.80 ppm (m, $-(OCH_2CH_2)_2OCH_2(CH_2)_8CH_3$, 8H), 3.96 ppm (t, $-CH_2CH_2O$–thiophene ring, 2H), 4.35 ppm (t, $-CH_2CH_2O$–thiophene ring, 2H), 6.97 ppm (s, thiophene ring protons, 1H). ^{13}C NMR ($CDCl_3$, δ/ppm): 14.34 ($-CH_3$), 22.90 ($-CH_2CH_3$), 26.34–29.93 ($-CH_2(CH_2)_6CH_2CH_2CH_3$), 32.14 ($-CH_2CH_2CH_3$), 70.18 ($-OCH_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3$), 70.26 ($-OCH_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3$), 70.96–71.27 ($-OCH_2CH_2(OCH_2CH_2)_2O(CH_2)_9CH_3$), 71.79 ($-OCH_2(CH_2)_8CH_3$).

2.6. *Poly(3-{2-[2-(2-methyloxyethoxy)ethoxy]ethoxy}thiophene) (PM3ET)*

2,5-Dibromo-3-{2-[2-(2-methyloxyethoxy)ethoxy]ethoxy}thiophene was prepared from 3-{2-[2-(2-methyloxyethoxy)ethoxy]-ethoxy}thiophene using a published synthetic procedure [34]. 2,5-Dibromo-3-{2-[2-(2-methyloxyethoxy)ethoxy]ethoxy}thiophene (4.30 g, 10.6 mmol) was dissolved in THF (10.0 mL), methylmagnesium bromide, 3.0 M diethylether solution (1.27 g, 10.6 mmol) were added, and the mixture refluxed with stirring for 2 h. Then Ni(dppp)Cl_2 catalyst (0.06 g, 0.11 mmol) was added and refluxed for an additional 2 h. When polymerization was completed, the polymer was precipitated into methanol as above, and the black precipitate subsequently washed by Soxhlet extraction using hexane and H_2O for 24 h, respectively. The result was 1.04 g of product (40% yield). ^1H NMR ($CDCl_3$, δ/ppm): $\delta = 3.35$ (s, $-OCH_3$, 3H), 3.52–3.80 (m, $-CH_3(OCH_2CH_2)_2OCH_2CH_2O-$, 8H), 3.95 (t, $-CH_2CH_2O$–thiophene ring, 2H), 4.35 (t, $-CH_2CH_2O$–thiophene ring, 2H), 6.97 (s, thiophene ring proton, 1H). ^{13}C NMR ($CDCl_3$, δ/ppm): 58.63 ($-CH_3$), 69.56–70.61 ($(-OCH_2CH_2)_2OCH_2CH_2OCH_3$), 71.52 ($-CH_2OCH_3$).

2.7. *Preparation of 1D gold nanowire network in the polythiophene derivatives*

For the preparation of gold nanowire networks with uniform cross-sectional diameters of about 10 nm, $HAuCl_4$ (7 mg, 0.02 mmol) was added into 5 mL of THF containing 19 mg of PD3ET (0.05 mmol). One milliliter of aqueous sodium borohydride ($NaBH_4$, 8 mg, 0.2 mmol) was then added and the mixture stirred vigorously for 1 h. The product was precipitated into methanol and purified by several reprecipitations from THF solution into methanol. Gold nanomaterials with different sizes and shapes were obtained from the same procedure except the amount of water, $HAuCl_4$, and the polymer in the reactions. For transmission electron microscopy (TEM), the mixtures of the obtained gold nanomaterials and the polythiophene derivatives were dissolved in THF and a drop of the solution is placed onto a carbon-coated copper grid.

2.8. *Instrumentation*

^1H NMR and ^{13}C NMR spectra were produced by a Bruker Avance 500 (500 MHz). All NMR samples were dissolved in deuterated chloroform ($CDCl_3$). FT-IR spectra measurements were performed on a JASCO FT/IR-200 using the polymer samples spin coated on silicon wafers from THF solution. The silicon wafers were cleaned by piranha solution. Gel permeation chromatography (GPC) was used to determine the molecular weights and molecular weight distribution, M_w/M_n, of polymer samples with respect to polystyrene standards using THF as the eluent. TEM images were taken on a JEOL JEM-200CX operated at 200 keV.

3. Results and discussion

An amphiphilic polythiophene, poly(3-{2-[2-(2-decyloxy ethoxy)ethoxy]ethoxy}thiophene) (PD3ET) was synthesized via condensation polymerization using the Grignard metathesis method (GRIM), initially reported by McCullough et al. [35]. (Fig. 1).

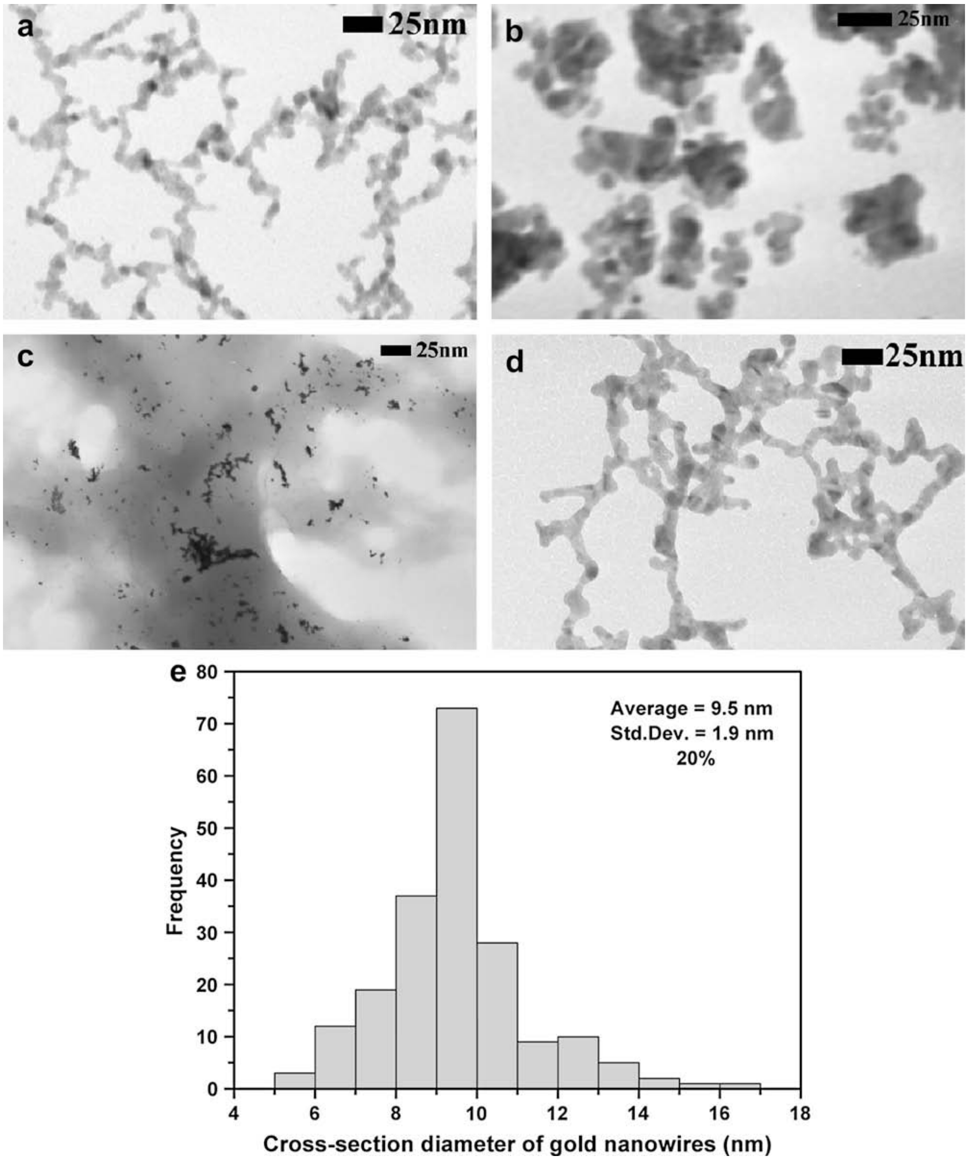

Fig. 6. TEM images of gold nanomaterials obtained using THF solution containing 0.04 mM $HAuCl_4$, 10 mM PD3ET and (a) 400 mM $NaBH_4$ aqueous solution, (b) 200 mM TBABH dissolved in THF solution. (c) TEM image of gold nanomaterials obtained using THF solution containing 4 mM $HAuCl_4$, 10 mM PD3ET, and 20 mM $NaBH_4$ aqueous solution. (d) TEM image of 2D gold nanowire networks obtained using THF solution containing 4 mM $HAuCl_4$, 10 mM regiorandom PD3ET, and 200 mM $NaBH_4$ aqueous solution. (e) Plot of frequency versus cross-sectional diameter for 200 randomly selected sections of the gold nanowire network as shown in Fig. 6(d).

3-{2-[2-(2-Decyloxyethoxy)ethoxy]ethoxy}thiophene was obtained by reacting 3-bromothiophene and tri(ethylene glycol) monodecyl ether with sodium methoxide using NMP as a solvent and CuBr as a catalyst, and then bromination of 3-{2-[2-(2-decyloxyethoxy)ethoxy]ethoxy}thiophene using NBS produced 2,5-dibromo-3-{2-[2-(2-methyloxyethoxy)ethoxy]ethoxy}thiophene. Finally, PD3ET was obtained by the polymerization of 2,5-dibromo-3-{2-[2-(2-methyloxyethoxy)ethoxy]ethoxy}thiophene using methylmagnesium bromide. PD3ET exhibits good solubility in common organic solvents, such as chloroform, dichloromethane, and tetrahydrofuran, and also in aprotic polar solvents, such as *N*-methyl-2-pyrrolidone, dimethylformamide, and others.

The chemical structure of PD3ET was confirmed by its ^{1}H NMR and ^{13}C NMR spectra, shown in Fig. 2. One sharp aromatic peak at $\delta = 6.96$ ppm from the proton of the thiophene ring in the ^{1}H NMR spectrum (h in Fig. 2(a)) and four peaks at $\delta = 111.7$, 113.2, 132.5, and 153.4 ppm in the aromatic region in the ^{13}C NMR spectrum (Fig. 2(b)) were observed. This result indicates that PD3ET having a regioregular structure with more than 95% head to tail sequence was obtained from the GRIM polymerization as reported by others [36]. The number average molecular weight and the molecular weight distribution of PD3ET calculated by GPC with polystyrene standards were 43,000 g/mol and 1.6, respectively.

Fig. 3 shows the FT-IR spectra of a PD3ET film and a PD3ET/$HAuCl_4$ mixture film on Si-wafer. For the mixture films, the molar ratio of gold salt to the monomeric unit in PD3ET, $[HAuCl_4]/[D3ET]$, was 0.4:1, which was the composition used for the preparation of nanowire networks having uniform wire diameter shown later in this discussion. The peak positions of the C–H stretching band of the polymer and the mixture films at 2852, 2925, and 2956 cm^{-1} are identical, while peak shifts of the C–O–C bands in the range of 1000 cm^{-1} and 1300 cm^{-1} were observed. The peak shift can be ascribed to the interactions between oxide groups in the side chain of PD3ET and metal ions because similar peak shifts due to ion–

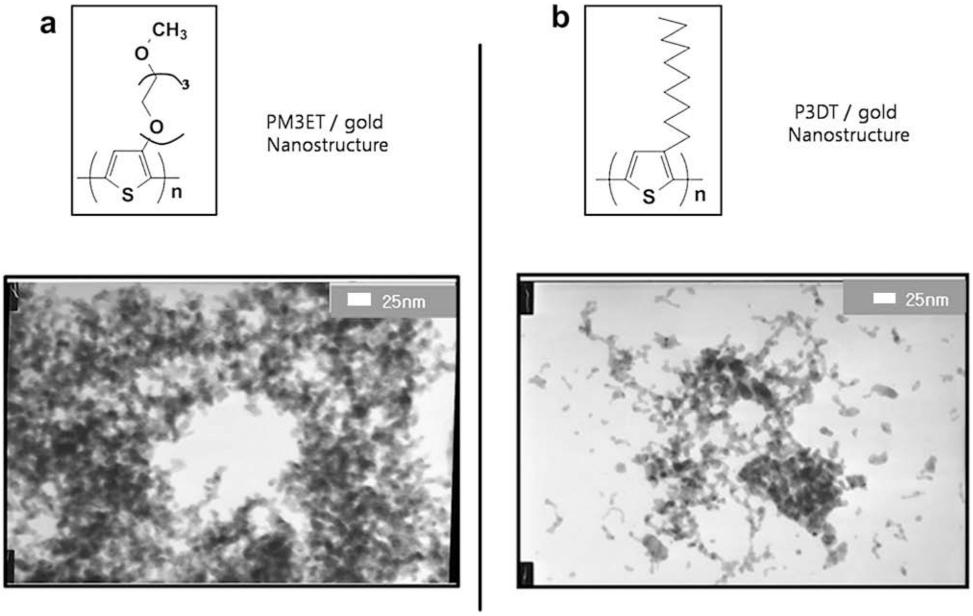

Fig. 7. TEM images of gold nanomaterials obtained by using 200 mM $NaBH_4$ aqueous solution and (a) 4 mM $HAuCl_4$, 10 mM PM3ET; (b) 4 mM $HAuCl_4$, 10 mM P3DT in THF solution.

dipole interactions have been reported previously [37–39]. Therefore, gold ions in $HAuCl_4$ can be coordinated with oxide groups in the side chains of PD3ET in the bulk state.

Since $NaBH_4$ is insoluble or only slightly soluble in THF, an aqueous solution of $NaBH_4$ was used to reduce $HAuCl_4$ mixed with THF solution of PD3ET. The amounts of all components such as $NaBH_4$, water, $HAuCl_4$, PD3ET, and THF, were observed to affect the size and shape of the gold nanomaterials. When 1.0 mL aqueous solution containing 0.2 mmol of $NaBH_4$ was added into 5 mL of a THF solution containing 0.02 mmol of $HAuCl_4$ and 0.05 mmol of PD3ET ($[HAuCl_4]/[D3ET] = 0.40$), gold nanowire networks having uniform cross-sectional diameter of about 10 ± 2.0 nm were obtained (Fig. 4). The gold nanowires have uniform diameters with the ratio of the standard deviation to the average diameter of 20%. The electron and X-ray diffraction patterns of gold nanowire networks showed scattering points corresponding to (111), (200), (220), (311) and (420) reflections for gold crystals.

The molar ratio of $HAuCl_4$ to the monomeric unit in PD3ET ($[HAuCl_4]/[D3ET]$) was varied to investigate the effect of the amount of the salt or polymer on the formation of the gold nanomaterials when the amount of reducing reagent was fixed to 1.0 mL aqueous solution containing 0.2 mmol of $NaBH_4$. If only a small amount of gold salt, such as 5 mL of the THF solution containing 0.0005 mmol of $HAuCl_4$ and 0.05 mmol of PD3ET ($[HAuCl_4]/[D3ET] = 0.01$), was used, gold nanomaterials with irregular shapes, an average length of 4–5 nm, and poorly connected gold networks were obtained, as shown in Fig. 5(a). When the amount of gold salt was increased from $[HAuCl_4]/[D3ET] = 0.10$ to 0.40, the cross-sectional diameter of the networks increased. The average cross-sectional diameter of the networks obtained from $[HAuCl_4]/[D3ET]$ ratios of 0.10, 0.40, and 0.80 is 6, 10, and 25 nm, respectively (Fig. 5).

When smaller amounts of water were used for preparing aqueous $NaBH_4$ solutions, loosely connected gold nanowire networks formed with smaller cross-sectional diameter. Fig. 6(a) shows the loosely connected gold nanowire networks with a cross-sectional diameter of about 6 nm obtained using 0.5 mL aqueous containing 0.2 mmol of $NaBH_4$ instead of the 1.0 mL aqueous solution used for the preparation of nanowire networks having

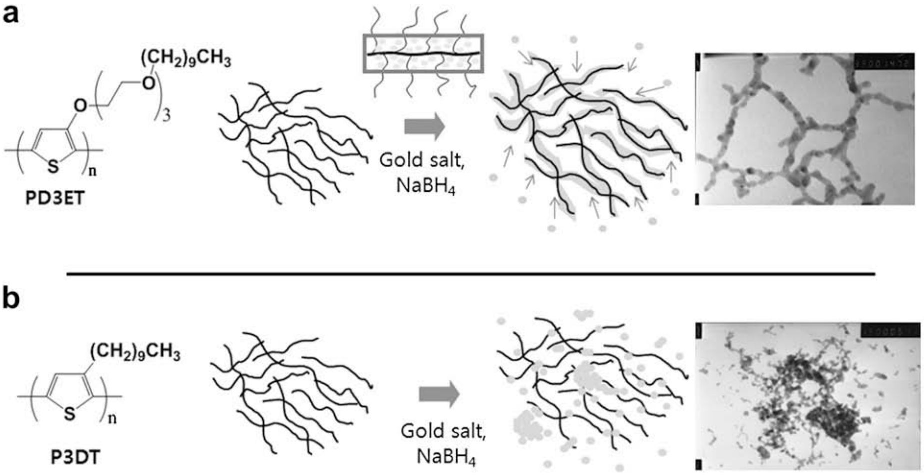

Fig. 8. Schematic illustration of the formation mechanism of the 2D gold nanowire networks by using (a) PD3ET/$HAuCl_4$, (b) P3DT/$HAuCl_4$.

cross-sectional diameter of 10 nm as in Fig. 5(c). Since PD3ET is not soluble in water, it is expected that the addition of water into polymer solution decreases the hydrodynamic volume of PD3ET. Therefore, less amount of water (0.5 mL) might expand the polymer chain in THF, leading to the formation of more expanded or loosely connected networks, more than the case when more water (1.0 mL) was used which leads to connected networks. When THF soluble reducing reagent, 0.2 mmol of tetrabutylammoniumborohydride (TBABH), was used to reduce $HAuCl_4$ in the THF solution of PD3ET in the absence of water, mostly disconnected gold nanomaterials were produced (Fig. 6(b)). Since TBABH can work as a surfactant such as phase transfer catalysts [33,40], the template structuring ability of the amphiphilic PD3ET to produce nanowire networks should be destroyed.

When 0.02 mmol of $NaBH_4$ instead of 0.2 mmol was added into the same THF solution as above, smaller gold nanomaterials with irregular shapes (Fig. 6(c)) were obtained, suggesting that the amount of reducing reagent used here was not enough to generate network structures. Also, when the amount of THF was increased ten times (0.05 mmol of PD3ET was dissolved in 50 mL of THF instead of 5 mL), then mostly disconnect gold nanomaterials similar to that in Fig. 5(a) were observed. Possibly, the high dilution of PD3ET by the large volume of THF destroyed the template structure of the polymer. Therefore, a certain ratio of water to THF is required to allow the template structure of PD3ET and an optimum amount of reducing agent, polymer, and gold salt is required to produce gold nanowire networks having uniform wire diameters.

We found that the stereoregularity of PD3ET does not affect the formation of nanowire network structures. To eliminate the effect of the molecular weight we intentionally prepared two PD3ETs having similar number molecular weights of 9900 and 10,800 g/mol, respectively, while they have quite different stereo-regioregularities such as 84% and 65%, respectively. Both polymers produced almost same gold nanowire networks. For example, when 1.0 mL of 200 mM $NaBH_4$ aqueous solution was added into 5 mL of THF solution containing 0.02 mmol of $HAuCl_4$ and 0.05 mmol of this regiorandom PD3ET ($[HAuCl_4]/[D3ET] = 0.40$, 65% stereoregularity), gold nanowire networks with uniform cross-sectional diameter of about 9.5 ± 1.8 nm were obtained by measuring 200 randomly selected sections of gold nanowires (Fig. 6(d)). The ratio of standard deviation to the average diameter is 20%. We also tried to observe the effect of cation of the gold salt on the formation of gold nanowire networks. When 0.02 mmol $LiAuCl_4$ instead of $HAuCl_4$ was added into THF solution containing regioregular PD3ET followed by reduction of gold ion using $NaBH_4$ as above procedure, gold nanowire networks similar to that in Fig. 6(d) were obtained.

Two polythiophene derivatives, PM3ET having hydrophilic methyltri(oxyethylene) side chains and poly(3-decylthiophene) having hydrophobic hydrocarbon chains, were used as templates for producing gold nanomaterials to examine the effect of the side chain polarity on the formation of the nanostructures. Mimicking the reaction conditions for the fabrication of gold nanowire networks which produced uniform cross-sectional diameter networks from PD3ET, when 5 mL of THF solution containing the gold salt and either of these two polymers ($[HAuCl_4]/[\text{monomer unit of polymer}] = 0.4$) and 1.0 mL of 0.2 mmol $NaBH_4$ aqueous solution were used, irregular shaped gold nanomaterials and/or aggregated nanowires structures were obtained as shown in Fig. 7. To produce gold nanowire network structures and/or well shaped gold nanomaterials, the ratio of gold salt to polymer or the amount of $NaBH_4$ aqueous solution used with these two polymers was varied. While hydrophilic PM3ET produced disconnected short nanowire and aggregated nanowires and hydrophobic poly(3-decylthiophene) produced mostly aggregated gold chunks, which clearly highlights the fact that the amphiphilic side chain structure of the polythiophene derivatives is a crucial factor for the formation of the gold nanowire network structures.

The formation mechanism of gold nanowire networks from PD3ET has been schematically constructed, as shown in Fig. 8(a). First, gold ions are selectively placed in the hydrophilic ethylene oxide units [41,42] around the polythiophene backbone through ion–dipole interactions. This was confirmed to some degree by measuring ^1H NMR of PD3ET/$HAuCl_4$ in THF-d_8. What we found was that, the proton peaks of (d)–(g) in Fig. 2(a) were broaden and shifted indicating the complex formation of gold salt with oxyethylene unit in the polymer. Similar peaks' shift and broadening were observed by others from the polymer and metal complexes [33,43]. When gold ions are reduced via a chemical reducing agent, $NaBH_4$, preliminary gold nanoparticles are produced *in situ* within the hydrophilic ethylene oxide structure and then these gold nanoparticles fuse into a wire network structure. Therefore, the hydrophilic nanochannel structure formed from the phase separation between hydrophilic oxyethylene unit and hydrophobic alkane unit in the side chain works as a template to produce the gold nanowire network along the nanochannel. However, when poly(3-decylthiophene) having only hydrophobic side groups and PM3ET with only hydrophilic side groups were used, such nanochannel structures working as a nanotemplate could not be generated. Then gold particle formation could not be organized along the polymer and only aggregated gold chunks were produced, as evidenced by gold materials located everywhere in the product (Fig. 8(b)).

4. Conclusion

Polythiophene having amphiphilic side group was successfully synthesized. It was established that the formation of gold nanowire networks was affected by the amount of $NaBH_4$, water, THF, gold salt, and the amphiphilic polythiophene employed. Specifically, gold nanowire networks having uniform diameter were produced when 0.2 mmol of $NaBH_4$ aqueous solution was added to 5 mL THF solution containing 0.02 mmol $HAuCl_4$ and 0.05 mmol of amphiphilic polythiophene. In these systems, wire diameter increased as the gold ion content increased. When polythiophenes having hydrophilic and hydrophobic side groups were used in the same reaction conditions instead of the amphiphilic polythiophene, irregular shaped gold nanomaterials and disconnected nanowire network structures were obtained, respectively. In conclusion, polythiophene/gold nanowire network composites were successfully synthesized using amphiphilic polythiophene as the template.

Acknowledgment

We thank the Korea Research Foundation through the Basic Research Program (Grant No. D00112) and the Korea Atomic Energy for Research Institute (KAERI). Experiments at Pohang Accelerator Laboratory were supported in part by MOST.

References

[1] Chabinyc ML. J Vac Sci Technol B 2008;26:445.
[2] Park YD, Kim DH, Lim JA, Cho JH, Jang Y, Lee WH, et al. J Phys Chem C 2008;112:1705.
[3] Shimizu Y, Kobayashi T, Nagase T, Naito H. Appl Phys Lett 2007;91:141909.
[4] Feng WD, Qi Zj, Sun YM. Eur Polym J 2007;43:3638.
[5] Wang Y, Zhou E, Liu Y, Xi H, Ye S, Wu W, et al. Chem Mater 2007;19:3361.
[6] Virginia R, Patrick GN, Stuart J, Pamela AT, Julie VM, Patrick RU. J Phys Chem 2005;109:19335.
[7] Oliveira MM, Castro EG, Canestraro CD, Zanchet D, Ugrate D, Roman LS, et al. J Phys Chem B 2006;110:17063.

[8] Kun H, Yuanjian Z, Yunze L, Junhua Y, Dongxue H, Zhijuan W, et al. Chem Eur J 2006;12:5314.
[9] Anna D, Shweta C, Michael K, Valeria N, Nandu C, Werner JB. Chem Mater 2007;19:4252.
[10] Gewu L, Chun L, Jiaoyan S, Zhaojia C, Gaoquan S. J Phys Chem C 2007;111:5926.
[11] Nadia G, Joachim L, Oren R, Cor EK. Chem Mater 2006;18:1089.
[12] Biplab KK, Sudip M, Sudip KB, Arun KN. Macromolecules 2007;40:278.
[13] Kim BS, Chen L, Gong J, Osada Y. Macromolecules 1999;32:3964.
[14] Milena G, Janis GM, Raoul C, George PS, Peter MF. Chem Mater 2006;18:6258.
[15] Mor GK, Shankar K, Paulose M, Varghese OK, Grimes CA. Appl Phys Lett 2007;91:152111.
[16] Greene LE, Law M, Yuhas BD, Yang P. J Phys Chem C 2007;111:18451.
[17] Feifei T, Mingyun G, Yiming Z, Li Z, Zheng X, Jun C. Cryst Growth Des 2008;8:2157.
[18] Park JH, Lim YT, Park OO, Kim JK, Yu JW, Kim YC. Chem Mater 2004;16:688.
[19] Peng CH, Wang HW, Kan SW, Shen MZ, Wei YM, Chen SY. J Magn Magn Mater 2004;284:113.
[20] Liu XG, Geng DY, Meng H, Shang PJ, Zhang D. Appl Phys Lett 2008;92:173117.
[21] Joseph Y, Peic A, Chen X, Michl J, Vossmeyer T, Yasuda A. J Phys Chem C 2007;111:12855.
[22] Zheng X, Guo D, Shao Y, Jia S, Xu S, Zhao B, et al. Langmuir 2008;24:4398.
[23] Kim JU, Cha SH, Shin KS, Jho JY, Lee JC. J Am Chem Soc 2005;127:9962.
[24] Cha SH, Kim JU, Kim KH, Lee JC. Chem Mater 2007;19:6297.
[25] Djalali R, Li SY, Schmidt M. Macromolecules 2002;35:4282.
[26] Yuan J, Drechsler M, Xu Y, Zhang M, Muller Axel HE. Polymer 2008;49:1547.
[27] Pei L, Mori K, Adachi M. Langmuir 2004;20:7837.
[28] Shen M, Du Y, Yang P, Jiang L. J Phys Chem Solids 2005;66:1628.
[29] Zhong Z, Luo J, Ang TP, Highfield J, Lin J, Gedanken A. J Phys Chem B 2004;108:18119.
[30] Song J, Garcia RM, Dorin RM, Wang H, Qiu Y, Coker EN, et al. Nano Lett 2007;7:3650.
[31] Lin B, Gelevs GA, Haber JA, Sundararaj U. Ind Eng Chem Res 2007;46:2487.
[32] Ramanath G, D'Arcy-Gall J, Maddanmimath T, Ellis AV, Ganesan PG, Goswami R, et al. Langmuir 2004;20:5583.
[33] Cha SH, Kim JU, Lee JC. Macromol Res 2008;16:711.
[34] Sheina EE, Khersonsky SM, Jones EG, McCullough RD. Chem Mater 2005;17:3317.
[35] Loewe RS, Khersonsky SM, McCullough RD. Adv Mater 1999;11:250.
[36] Chen TA, Wu X, Rieke RD. J Am Chem Soc 1995;117:233.
[37] Wahab SA, Matin MR, Matsuura H. J Mol Struct 2003;658:79.
[38] Dag O, Alayoglu S, Tura C, Celik O. Chem Mater 2003;15:2711.
[39] Lin JH, Woo EM, Huang YP. J Polym Sci Part B Polym Phys 2006;44:3357.
[40] Zeng R, Rong MZ, Zhang MQ, Liang HC, Zeng HM. J Mater Sci Lett 2001;20:1473.
[41] Kim JU, Cha SH, Shin KS, Jho JY, Lee JC. Adv Mater 2004;16:459.
[42] Sakai T, Alexandridis P. Langmuir 2005;21:8019.
[43] Shelley EJ, Ryan D, Johnson SR, Couillard M, Fitzmaurice D, Nellist PD, et al. Langmuir 2002;18:1791.