

Synthesis of T-Shaped Graft Copolymer and its Wire-like Micelle Formation

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Research Article

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ABSTRACT

Conjugated oligothiophene and polythiophene have attracted an enormous scientific attention because of their high charge-carrier mobility and unique structural properties. In this study, we synthesized amphiphilic T-shaped graft copolymers and examined the micellar behavior of them in aqueous solution. The T-shaped graft copolymers consist of a poly(ethylene glycol) block covalently bonded to the center of conjugated oligothiophenes. As the length of the oligothiophene units increased from terthiophene to quinquethiophene, the rigidity of backbone of the graft copolymers increased, resulting in the change of micellar structure from sphere to cylinder in aqueous solution. These results are in good accordance with our previous dynamics simulation results.

INTRODUCTION

Self-assembling ability of diblock copolymers has been received much attentions and offered a possibility to organize specific functions into nanometer domains with well-defined supramolecular architectures^[1-3]. Formation of diblock copolymers in which the one block is composed of a conjugated polymer chain can develop a new class of self-assembling electro-active materials, because of the unique optical and electrical properties of the conjugated polymers^[4-6]. The properties and performance of conjugated polymer do not only depend on the molecular structures themselves, but also on supramolecular characteristics such as the molecular packing of the conjugated polymer moieties. Various morphologies developed by the diblock copolymers based on the conjugated polymers have been utilized for the fabrication of novel electric and electro-optical devices^[7].

Among the various conjugated organic materials, oligothiophene and polythiophene are the most promising materials for various applications, such as organic transistor, light-emitting diodes, and organic photovoltaics, because of their highly favorable electro-optical features, such as a high charge-carrier mobility, small band gap, and high quantum yield for fluorescence^[8,9]. Recently, the well-controlled synthesis of regioregular poly(3-alkylthiophenes) has been developed by McCullough and widely utilized by many research groups to design and create the new polythiophene derivatives for various opto-electronic applications^[10-12]. Li et al has synthesized the polythiophene and poly(thienylene vinylene) derivatives having conjugated side chains to broaden the absorption band in the visible region^[13]. Jo et al has designed and synthesized a diblock copolymer based on regioregular polythiophene and fullerene derivatives as an active material for photovoltaic cells^[14,15]. In spite of the good solubility and high charge-carrier mobility of the polythiophene derivatives, the p-conjugated oligothiophenes have still attracted an enormous scientific attention due to their unique structural properties; particularly designed linear and cyclic oligothiophenes can self-assemble to form well-ordered 2D nanostructures^[16].

In our previous research, we have investigated the effect of chain rigidity on the micellar behavior of amphiphilic graft copolymer with a rigid backbone and a flexible side chain (T-shaped graft copolymer) by using Brownian dynamics simulation^[17]. From the simulation results, we have concluded that the rigidity of hydrophobic backbone of the T-shaped graft copolymer is a critical factor to form the well-ordered micellar structure in a hydrophilic solvent system. In this study, to verify and realize the simulation results with experimental data, the amphiphilic T-shaped graft copolymers, where a poly(ethylene glycol) (PEG) block were covalently bonded to the center of a conjugated oligothiophene moieties, were synthesized. The molecular structure and optical properties of the T-shaped graft copolymers were analyzed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy, nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), UV/vis, and fluorescence spectroscopy. The morphologies of the amphiphilic T-shaped graft copolymer were examined by using transmission electron microscopy (TEM).

MATERIALS AND METHODS

Materials

Poly(ethylene glycol) methyl ether (PEG-COOCH₃, Aldrich, Mn=2000 g/mol), 4-(Dimethylamino)pyridine (DMAP, Aldrich, 99%), and Methylene chloride (Daejung Chemicals and Metals) were purified before use by precipitation, recrystallization, and distillation, respectively, using the previously reported methods [18].

Synthesis of Terthiophene-PEG (3TN-PEG)

3TN-PEG was synthesized from 2Br-1TN-PEG via Stille coupling with 2-(tributylstannyl)-thiophene, using the previously reported methods [18].

Synthesis of Quinquethiophene-PEG (5TN-PEG)

5TN-PEG was synthesized from 3TN-PEG via NBS bromination and Stille coupling with 2-(tributylstannyl)-thiophene, using the previously reported methods [18].

Characterization

The molecular structure of the synthesized graft copolymers was characterized by a 300 MHz 1H NMR spectrometer (Bruker, Avance DPX-300). The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) were calculated from a size exclusion chromatography (SEC, Waters 150C) profiles (calibration with standard polystyrene). A MALDI-TOF data were recorded with a Voyager-DETM STR Biospectrometry Workstation. TEM (Hitachi H-600) observations were performed with an acceleration voltage of 50 kV in bright field. UV-Vis absorption spectra were recorded on a HP 8452A spectrometer. A Fluorescence spectra were recorded with a fluorescence spectrometer (RF 5301, Shimadzu).

RESULTS

Synthesis of T-shaped Graft Copolymers

Figure 1 shows the overall synthetic processes of amphiphilic T-shaped graft copolymers. To investigate the effect of length of rigid backbone of non-linear copolymer on the micellar structure, two kinds of amphiphilic T-shaped graft copolymers were synthesized, where the PEG was grafted on the center of terthiophene and quinquethiophene backbone as a flexible and water-soluble side chain. Because the oligothiophenes have poor solubility in most of solvents without side chains, they were synthesized after PEG was grafted onto 2,5-dibromo-thiophene (2Br-1TN). Terthiophene-terminated PEG (3TN-PEG) and quinquethiophene-terminated PEG (5TN-PEG) were synthesized via the method previously reported by our group [18]. The resulting 3TN-PEG and 5TN-PEG are well soluble in organic solvents, such as chloroform, THF, Toluene, DMF, DMSO and even H₂O owing to the PEG graft polymer.

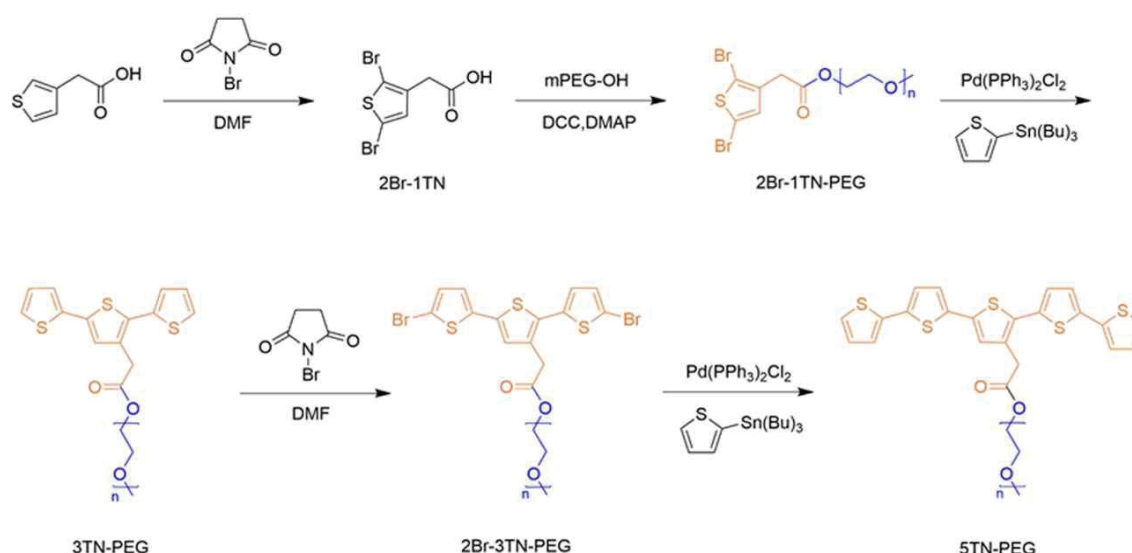


Figure 1. Synthesis route of 3TN-PEG and 5TN-PEG.

The molecular structures of 2Br-1TN-PEG, 3TN-PEG, and 5TN-PEG were characterized by using ¹H NMR spectra (**Figure 2**). Methyl protons in PEG chain and thiophene protons were clearly observed at δ =3.4-3.6 and 7.1-7.6 ppm, respectively, in the NMR spectra of 2Br-1TN-PEG and 3TN-PEG. By comparing the integration of these peaks, we could confirm that 2,5-dibromothiophene and terthiophene were perfectly combined to the end of PEG chain. Comparison of integration between the quinquethiophene protons and methyl protons in PEG also confirms the 5TN-PEG was successfully synthesized by NBS bromination and Stille coupling reaction from 3TN-PEG (**Figure 2**).

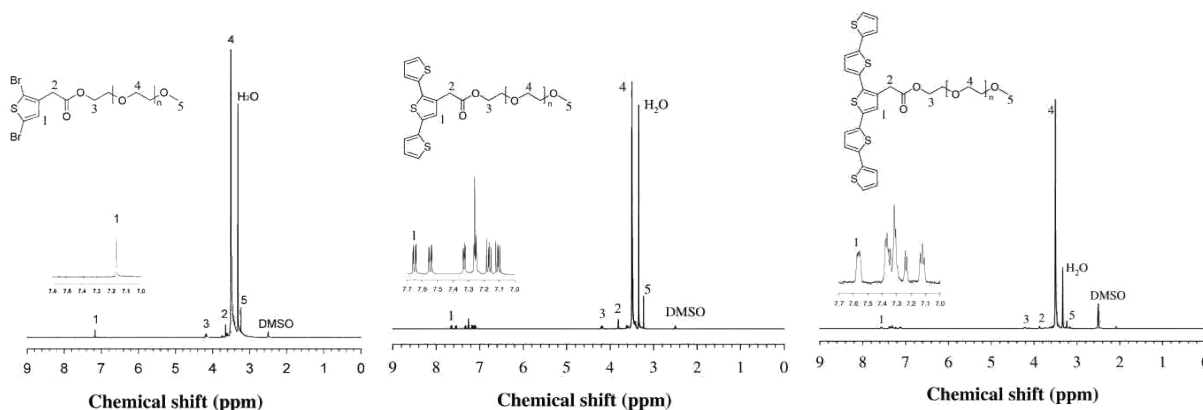


Figure 2: ¹H NMR spectra of 2Br-1TN-PEG, 3TN-PEG and 5TN-PEG in DMSO.

Figure 3 shows the SEC traces of the PEG, 3TN-PEG, and 5TN-PEG. Both 3TN-PEG and 5TN-PEG exhibit unimodal peak with narrow molecular weight distribution ($M_n=2,300$, $M_w/M_n=1.03$ for 3TN-PEG and $M_n=2,500$, $M_w/M_n=1.03$ for 5TN-PEG). To evaluate the molecular weight of the graft copolymers more exactly, we carried out a MALDI-TOF MS analysis, which displays that the number average molecular weights of 3TN-PEG and 5TN-PEG are 2280 and 2450 g mol^{-1} , respectively, as shown in **Figure 4**. The difference of molecular weight (170 g mol^{-1}) between 3TN-PEG and 5TN-PEG clearly reveals that the two more thiophenes were attached to the terthiophene backbone of 3TN-PEG to form the 5TN-PEG graft copolymer.

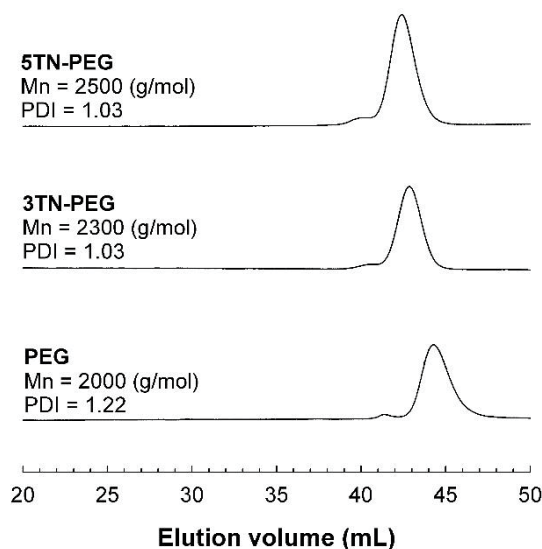


Figure 3. SEC traces of PEG, 3TN-PEG, and 5TN-PEG.

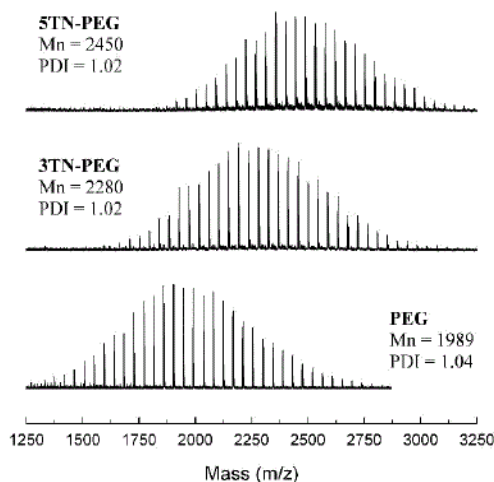


Figure 4. MALDI-TOF MS spectra of PEG, 3TN-PEG, and 5TN-PEG

Optical Properties of T-Shaped Graft Copolymers

UV-visible absorption spectra of 3TN-PEG and 5TN-PEG in H₂O are given in **Figure 5**. The aqueous solution of 3TN-PEG (1 mg/mL) shows yellow color and UV-visible spectrum of it has a maximum absorption peak at 350 nm, corresponding to the absorption of terthiophene, whereas the transparent aqueous solution of PEG does not exhibit any absorption peak. The absorbance of the orange-colored aqueous solution of 5TN-PEG shows a red-shift with a substantial increase of absorption, as compared with that of 3TN-PEG even at the same concentration (1 mg/mL).

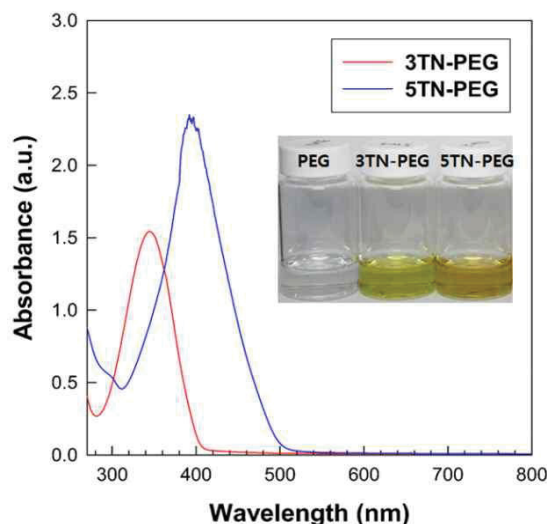


Figure 5. UV-vis absorption spectra of 3TN-PEG, and 5TN-PEG. Inset is the images of aqueous solutions of PEG, 3TN-PEG, and 5TN-PEG (1 mg/mL).

Figure 6 shows the fluorescence spectra of aqueous solutions of 3TN-PEG and 5TN-PEG at 1 mg/mL and 5 mg/mL concentration, respectively. At the lower concentration (1 mg/mL), the fluorescence spectra of 3TN-PEG and 5TN-PEG have maximum at 490 and 540 nm, respectively, and show characteristic vibronic structure. From the observed high fluorescence intensity, we found that the T-shaped graft copolymers were molecularly dissolved in aqueous solution. However, the fluorescence intensity of both solutions at 5 mg/mL was drastically reduced when compared to low concentration solutions, which confirms that 3TN-PEG and 5TN-PEG copolymers form aggregates at higher concentration in aqueous solution ^[19].

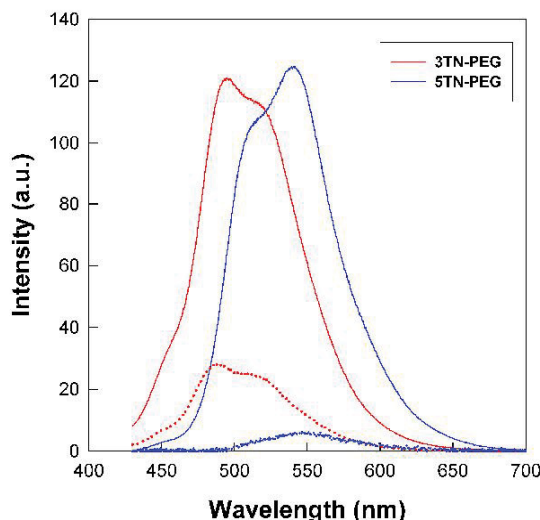


Figure 6. Fluorescence spectra of aqueous solution of 3TN-PEG (red line) and 5TN-PEG (blue line) at 1 mg/mL (solid line) and 5 mg/mL (dotted line).

Micelle Formation of T-shaped Graft Copolymers

Figure 7 shows the TEM images of micelles developed from aqueous solutions of 3TN-PEG and 5TN-PEG. Aqueous solution with higher concentration than 5 mg/mL exhibits well-defined micelle structure. It is noted that the 3TN-PEG graft copolymer shows a sphere structure, whereas the 5TN-PEG forms cylindrical micelles in H₂O. The spherical micelles from 3TN-PEG had uniform size distribution of 2~3 nm and were distributed very homogeneously in aqueous solution (**Figure 7a**). When the concentration of 3TN-PEG in aqueous solution was increased from 5 to 10 mg/mL, the density of micelles was increased, whereas the size of them was not changed significantly (Supporting information). Whereas, the 5TN-PEG graft copolymer showed the cylinder-type micellar structures with 100-300 nm length, and 15-20 nm diameter, respectively (**Figure 7b**).

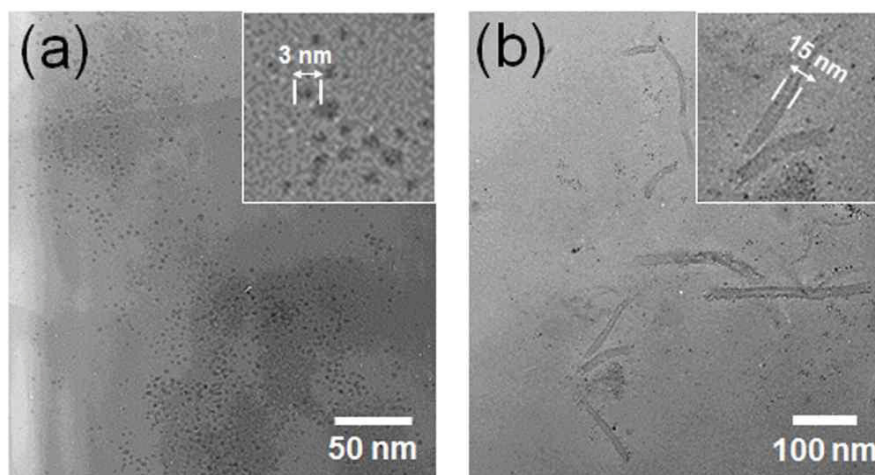


Figure 7. TEM images of aqueous solutions of (a) 3TN-PEG and (b) 5TN-PEG at 5 mg/mL.

The unique micellar behavior of the T-shaped graft copolymers can be explained using a Brownian dynamics simulation carried out by our group^[17], in which the effect of chain rigidity on the formation of micelle structures of amphiphilic graft copolymer with a hard backbone and a soft side chain was investigated. From the dynamics simulation, we have found that the T-shaped graft copolymer can form both spherical and cylindrical micelles, depending on the rigidity of hydrophobic backbone in a hydrophilic solvent system. The graft copolymers with flexible backbone form spherical micelles due to the hairpin-like structure of flexible backbone in the core of micelle, while the rigid backbone chains are stacked with stretched conformation, which results in the wire-like micelles. In our experimental cases, as the length of the oligothiophene increased from terthiophene (3TN-PEG) to quinquethiophene (5TN-PEG), the rigidity of backbone increased, resulting in the change of micellar morphologies from sphere to cylinder, as shown in

From the simulation results, the second critical factor is the grafting position of flexible side chain onto the rigid backbone; as the grafting point is shifted from center to edge of the backbone, the long cylindrical micelles were broken into separate aggregates, which is why the cylindrical micelle has not been well observed in flexible block copolymer system (**Figure 8**).

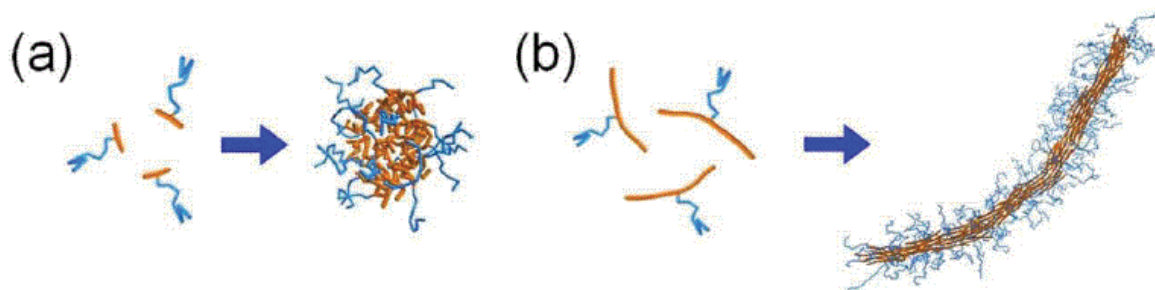


Figure 8. Micelle formation of (a) 3TN-PEG and (b) 5TN-PEG graft copolymers in aqueous solution. Orange rod and blue pendant mean the oligothiophene backbones and PEG side chain, respectively.

CONCLUSIONS

In summary, we synthesized amphiphilic T-shaped graft copolymers and examined the micellar behavior of them in H₂O. The T-shaped graft copolymers consist of a poly(ethylene glycol) block covalently bonded to the center of conductive oligothiophenes. Two kinds of T-shaped graft copolymers, 3TN-PEG and 5TN-PEG, were synthesized via NBS bromination and Stille coupling reaction from the PEG-grafted thiophene moieties. From the UV-vis and fluorescence spectroscopy data, we confirmed that the T-shaped graft copolymers form polymeric aggregates in H₂O at a concentration of 5.0 mg/mL. The 3TN-PEG graft copolymer shows a spherical micelle structure, whereas the 5TN-PEG forms cylindrical micelles in H₂O. As the length of the oligothiophene units increased from terthiophene to quinquethiophene, the rigidity of backbone of the graft copolymers increased, resulting in the change of micellar structure from sphere to cylinder in aqueous solution. This phenomenon is in good accordance with our previous dynamics simulation results.

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AUTHOR CONTRIBUTION

Jea Uk Lee planned and performed the experiments, and wrote the manuscript.

CONFLICT OF INTEREST

The author declare no conflict of interest.

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