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Fluorescent conjugated polymer nanoparticles and aggregates based on rapid precipitation and self-assembled π -conjugated systems



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HIGHLIGHTS

- Copolymers containing fluorene and diphenylamine with different chains have been prepared.
- Conjugated polymer nanoparticles have been prepared in the aqueous media.
- Polymers with micrometer sized particles were obtained from solvent diffusion method.
- Self-assembled polymers exhibited a relatively high photoluminescence quantum yield.

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ABSTRACT

Conjugated copolymers containing fluorene and diphenylamine moieties with octyl and triethylene glycol side chains have been synthesized via Suzuki-Miyaura cross-coupling reaction and their structures have been characterized. Conjugated polymer nanoparticles and self-organization of the polymers have been prepared by rapid precipitation and solvent diffusion methods, respectively. The conjugated polymers exhibited well-defined spherical amorphous structures and crystalline microspheres with a diameter ranging from several nanometer to micrometer. Self-assembled conjugated polymer aggregates were obtained in a selective good solvent/poor solvent mixture. Alternating conjugated polymers are generally difficult to assemble into well-defined spheres due to their rigid and planar backbones, however, alternating polymers containing dioctyl and triethylene glycol side chains tends to form microspheres or sheet-like structures depending on the different solvent mixtures. The emission maximum of the dispersed polymers in water was significantly red-shifted with a dramatic reduction in the photoluminescence quantum yield. In addition, the emission maximum of the self-assembled cooplymers was barely red shifted with a small reduction in the photoluminescence quantum yield.

1. Introduction

Nanometer-sized particles have attracted much attention due to their tremendous applications such as drug and gene delivery [1], biosensors [2], gas sensors [3], fluorescence imaging and cellular tracking [4,5]. Molecular self-assemblies have an intriguing role in nature such as the formation of molecular crystals and the formation of an ordered array of supramolecular architectures by the interaction of noncovalent forces [6,7]. The interactions of self-assembled supra-molecules include ionic, hydrogen and coordination bonds as well as dispersion and van der Waals forces which lead to ordered nanostructures upon equilibration between aggregated and non-aggregated states [8,9]. Self-assembled polymer colloids can be prepared by either direct polymerization from the corresponding monomers or post polymerization techniques such as vapor diffusion method, interface precipitation method and miniemulsion method [10–16]. The different solubility of the hydrophilic and hydrophobic segments of the amphiphilic copolymers in organic solvents have a tendency to induce self-assembly into micelles in a selected solvent [17,18]. Hydrophilic components such as polymers containing oligo(ethylene glycol) chains have been widely applied in cosmetic and pharmaceutic applications due to their biocompatibility and non-toxicity.

The preparation and design of novel π -conjugated backbones offer challenges to improve the device performance as the solubility is decreased through the strong $\pi - \pi$ interactions in the solid state. In order to overcome this issue, flexible side chains are usually introduced to afford better solubility for enhanced device fabrication [19,20]. The solubility as well as optoelectronic application of the conjugated polymers were maintained by equipping a rigid conjugated polymer backbone with an alkyl side chain such as oligo(ethylene glycol) chains

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and fluoroalkyl chains [19,21] for efficient organic light emitting diodes, organic field-effect transistors and organic photovoltaics devices which can be deposited in polar nonhalogenated solvents [22,23]. The introduction of alkyl chains to the organic materials increases van der Waals interactions between these chains and the solvent. This increases the total interaction energy between the organic molecules and solvent as well as the vibrational motions of alkyl chains that may destroy the molecular arrangement in the solid state by decreasing the interactions between π -conjugated systems [20]. Oligo(ethylene glycol) chains are well known for their hydrophilic properties due to many ether groups [24] and is often used to increase molecule/polymer solubility in water or polar organic solvents [25,26]. The side-chain-end functionalities of conjugated polymers in water/polar organic solvent mixtures are one of the important classes of polymers which can be processed from water or other polar solvents for interface modification of organic electronics [27]. As mentioned by B. Meng and co-worker [28], oligo(ethylene glycol) chains are more flexible than alkyl chains due to less steric hindrance between the two lone electron pairs in two oxygen atoms [29]. The nature of the flexible side chains on conjugated polymer backbones alter the optical, electronic and charge transport behavior by the self-organization of polymer backbones in the solid state [30,31]. A high degree of solubility of the polymers in common organic solvents may increase the molecular weight during the polymerization and enhance the processability of thin films [32,33].

The synthetic design of the dispersible nanoparticles of the π -conjugated polymers in aqueous systems is still a big challenge for fluorescence imaging because of the aggregation of the hydrophobic components in aqueous media decreasing the light harvesting ability of the polymers. Previously, we have successfully prepared alternating copolymers containing fluorenes, PEGylated carbazoles and diphenylamines by Suzuki-Miyaura cross-coupling reaction and their dispersion nanoparticles in aqueous media [34]. Although the self-organized structures of the polyfluorenes [35-40] and the photophysical properties of the amphiphilic polyfluorenes [41–45] have been intensively investigated, there is no report on the alkyl and tri(ethylene glycol) substituted fluorene and diphenylamine copolymers. Herein, we report the synthesis of fluorescent conjugated polymers containing tri(ethylene glycol) and octyl side chains with various segments through Suzuki-Miyaura cross-coupling reaction and their structural characterizations. The optical properties of the as prepared polymers in water dispersion and self-organization from good solvent/poor solvent mixtures were studied. The particle sizes, morphologies and self-organization of the conjugated polymers were also investigated.

2. Experimental section

Materials and instrumentation. Chemicals, reagents and solvents from commercial sources were analytical or spectrophotometric grade and used without further purification unless otherwise noted. ¹H nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker 600 MHz. Chemical shifts are reported in ppm relative to the indicated residual solvent. All coupling constants (J values) are reported in hertz (Hz) and the following abbreviations are used to indicate multiplicity: s = singlet, d = doublet, dd = doublet of doublets, t = triplet and m = multiplet, br = broad signals. Molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters ACQUITY Advanced Polymer Chromatography with RI detector in THF solution calibrated with low polydispersity polystyrene standards. The flow rate was set as a 0.8 mL/min in 45 °C. The UV-vis absorption spectra were recorded using a Jasco (V-670) UV-Vis-NIR spectrophotometer and fluorescence spectra were recorded a Jasco FP-8500 fluorescence spectrophotometer. The fluorescence quantum yields (Φ) of the conjugated polymers and conjugated polymer nanoparticles were performed in THF and water solutions, respectively, relative to the quinine sulfate ($\Phi = 54.6\%$ in 0.1 MH₂SO₄) as a standard. The hydrodynamic size of the nanoparticle dispersions were measured using a Malvern Zetasizer Nano ZS at a temperature of 25 °C. The SEM images of the conjugated polymer nanoparticles were obtained by field-emission scanning electron microscopy (FESEM, JSM 6500F, JEOL).

Synthesis of 2,7-dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9Hfluorene (M1). A solution of 1-(2-(2-methoxyethoxy)ethoxy)-2-bromoethane (6.08 g, 26.8 mmol), 2,7-dibromofluorene (4.00 g, 12.4 mmol) and potassium iodide (67.60 mg, 0.27 mmol) in dimethyl sulfoxide (40 mL) was cooled to 0 °C under a nitrogen atmosphere. Potassium hydroxide (2.28 g, 40.8 mmol) was added to the mixture and the mixture was allowed to warm to room temperature and was stirred for 16 h. The reaction mixture was then poured into water and extracted with ethyl acetate and the organic layers dried under reduced pressure. The crude product was purified by silica column chromatography, eluting with ethyl acetate/hexane (2:3) to give a colorless solid (4.94 g, 65%). ¹H NMR (600 MHz, CDCl₃): δ 7.52 (d, J = 1.8 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.46 (dd, J = 8.4, 1.8 Hz, 2H), 3.52 (m, 4H), 3.48 (m, 4H), 3.38 (m, 4H), 3.33 (s, 6H), 3.20 (m, 4H), 2.78 (t, J = 7.2 Hz, 4H), 2.34 (t, J = 7.2 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃ δ): 150.95, 138.46, 130.66, 126.72, 121.64, 121.21, 71.88, 70.48, 70.45, 70.06, 66.79, 58.99, 51.91, 39.49. HR-MS (EI, [M]⁺): calculated for $[C_{27}H_{36}Br_2O_6]^+$: *m/z* 614.0879, found *m/z* 614.0879.

Synthesis of N-octyl-4,4'-dibromodiphenylamine (M2). A mixture of bis(4-bromophenyl)amine) (4.90 g, 15.0 mmol), potassium tert-butoxide (2.02 g, 18.0 mmol) and 120 mL of anhydrous THF was stirred for 30 min at room temperature under a nitrogen atmosphere. 1-Bromooctane (63.47g, 18.0 mmol) was added and the mixture was stirred for 24 h at 60 $^{\circ}\mathrm{C}.$ After cooling to room temperature, the reaction mixture was poured into water and then extracted with dichloromethane. The combined organic layers were washed with water several times and dried over anhydrous MgSO4. The crude product was purified by column chromatography (hexane/DCM) 7:3, v/v) to give a colorless oil (5.25 g, 80%). ¹H NMR (600 MHz, CDCl₃): δ 7.37 (d, J = 8.4 Hz, 4H), 6.87 (d, J = 8.4 Hz, 4H), 3.64 (m, 2H), 1.65 (m, 2H), 1.32–1.27 (m, 10H), 0.87 (t, J = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃ δ): 146.77, 132.27, 122.57, 113.86, 52.45, 31.78, 29.35, 29.25, 27.26, 27.01, 22.62, 14.08. HR-MS (EI, [M]+): calculated for $[C_{20}H_{25}Br_2N]^+$: *m*/z 437.0354, found *m*/z 437.0352.

Synthesis of 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-octyl diphenylamine (M3). To a solution of N-octyl-4,4'-dibromodiphenylamine (5.0 g, 11.3 mmol) in anhydrous THF (150 mL) was added dropwise 11.8 mL (29.4 mmol) of n-butyllithium (2.5 M in hexane) at -78 °C under a nitrogen atmosphere. After the mixture was stirred for 2 h at -78°C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.4 g, 45.2 mmol) was added and the mixture was warmed to room temperature and stirred overnight. The resulting mixture was poured into water, extracted with ether, and then dried over anhydrous MgSO₄. After the evaporation of the solvent, the crude product was recrystallized from hexane and dried under vacuum to give white crystals (yield 3.70 g, 60%). ¹H NMR (600 MHz, CDCl₃): δ 7.70 (d, J = 8.4 Hz, 4H), 7.00 (d, J = 8.4 Hz, 4H), 3.72 (m, 2H), 1.65 (t, J = 7.8 Hz, 2H), 1.28 (s, 24H), 1.27–1.22 (m, 10H), 0.88 (t, J = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃, δ): 150.11, 136.04, 119.96, 83.51, 52.06, 31.79, 29.34, 29.24, 27.40, 27.01, 24.86, 22.62, 14.08. HR-MS (EI, $[M]^+$): calculated for $[C_{32}H_{49}Br_2NO_4]^+$: m/z 533.3848, found m/z533.3850.

Synthesis of 4-bromo-*N*-(4-bromophenyl)-*N*-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)aniline **(M4)**. Bis(4-bromophenyl) amine (4.0 g, 12.30 mmol) and potassium hydroxide powder (3.45 g, 61.50 mmol) were dissolved in 50 mL of dimethyl sulfoxide. A solution of 1-(2-(2methoxyethoxy)ethoxy)-2-bromoethane (TEG-Br) (4.0 g, 18.0 mmol) in 10 mL DMSO was added dropwise by syringe and stirred for 36 h at room temperature. After quenching the reaction mixture by the addition of distilled water, the crude compound was extracted with ethyl acetate and washed with brine. The combined organic layers were dried over MgSO₄ and concentrated using a rotary evaporator. The crude compound was purified by column chromatography with hexane/EA (7:3) as the eluent to give the pure compound in a yield of 3.47 g (60%). ¹H NMR (600 MHz, CDCl₃, δ): 7.33 (d, 4H, *J* = 9.0 Hz), 6.91 (d, 4H, *J* = 9.0 Hz), 3.86 (t, 2H, *J* = 6.0 Hz), 3.64 (t, 2H, *J* = 6.0 Hz), 3.58–3.59 (m, 6H), 3.50 (m, 2H), 3.36 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, δ): 146.55, 132.24, 122.74, 114.11, 71.91, 70.75, 70.68, 70.61, 68.01, 59.04, 51.78. HR-MS (EI, [M]⁺): calculated for [C₁₉H₂₃Br₂NO₃]⁺: *m/z* 471.0045, found *m/z* 471.0044.

Synthesis of the alternating copolymer P1: 2,7-dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9H-fluorene (M1) (0.37 g, 0.60 mmol), 4,4'bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-N-octyl diphenylamine (M3) (0.32 g, 0.60 mmol) and a drop of Aliquat 336 were dissolved in toluene (12 mL) and then the mixture was degassed for 30 min. A tetrakis (triphenylphosphine) palladium (0) (35 mg. 0.03 mmol) was added to the reaction mixture followed by the addition of aqueous sodium carbonate (2 M, 6 mL) and was degassed for an additional 30 min. The reaction mixture was stirred and heated at reflux for 56 h before cooling to room temperature. The resulting polymer was precipitated by pouring into distilled water; the crude compound was extracted with dichloromethane, washed with brine, and dried over MgSO₄. The solvent was removed in vacuo and the resulting crude powder was purified by Soxhlet extraction with methanol and acetone for a day before redissolving in chloroform. The solid was then dried under vacuum to give a yield of 60%. ¹H NMR (600 MHz, $CDCl_3$, δ): 7.74 (d, 2H), 7.65–7.60 (m, 8H), 7.17 (d, 4H), 3.80 (br, 2H), 3.50–3.49 (m, 4H), 3.45-3.43 (m, 4H), 3.40 (t, 4H), 3.30 (s, 6H), 3.24 (t, 4H), 2.86 (t, 4H), 2.47 (br, 4H), 1.70 (br, 2H), 1.31-1.29 (m, 10H), 0.89 (t, 3H). Mn = 20,800, Mw = 40,200, PDI = 1.93.

Synthesis of the alternating copolymer **P2**: A similar procedure was used as that described for the synthesis of **P1** using 2,7-dibromo-9,9-bis (2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (**M1**) (0.18 g, 0.30 mmol), *N*-octyl-4,4'-dibromodiphenylamine (**M2**) (0.13g, 0.30 mmol), 4,4'-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-*N*-octyl diphenylamine (**M3**) (0.32 g, 0.60 mmol), a drop of Aliquat 336 and tetrakis (triphenylphosphine) palladium (0) (35 mg, 0.03 mmol). **P2** was obtained in a yield of 47%. ¹H NMR (600 MHz, CDCl₃, δ): 7.74–7.72 (br, 2H), 7.64–7.60 (m, 8H), 7.52–7.50 (br, 8H), 7.17–7.09 (m, 12H), 3.78–3.76 (br, 6H), 3.50–3.49 (m, 4H), 3.45–3.44 (m, 4H), 3.41–3.39 (m, 4H), 3.30 (t, 6H), 3.24 (t, 4H), 2.86 (br, 4H), 2.47 (br, 4H), 1.74 (br, 6H), 1.32–1.28 (m, 30H), 0.89–0.88 (m, 9H). Mn = 8000, Mw = 10,600, PDI = 1.33.

Synthesis of the alternating copolymer **P3**: A similar procedure was used as that described for the synthesis of **P1** using 2,7-dibromo-9,9-bis (2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (**M1**) (0.18 g, 0.30 mmol), 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-*N*-octyl diphenylamine (**M3**) (0.32 g, 0.60 mmol), 4-bromo-*N*-(4-bromophenyl)-*N*-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)aniline (**M4**) (0.14 g, 0.30 mmol), a drop of Aliquat 336 and tetrakis (triphenylphosphine) palladium (0) (35 mg, 0.03 mmol). **P3** was obtained in a yield of 43%. ¹H NMR (600 MHz, CDCl₃, δ): 7.74–7.73 (br, 2H), 7.64–7.60 (m, 8H), 7.53–7.50 (m, 8H), 7.17–7.12 (m, 12H), 4.02 (br, 4H), 3.76 (br, 4H), 3.65–3.62 (m, 4H), 3.54–3.53 (br, 2H), 3.50–3.48 (m, 4H), 3.45–3.43 (m, 4H), 3.41–3.39 (m, 4H), 3.37–3.36 (m, 2H), 3.30 (t, 9H), 3.25–3.23 (m, 4H), 2.86 (br, 4H), 2.47 (br, 4H), 1.75 (br, 4H), 1.32–1.29 (m, 20H), 0.88 (t, 6H). Mn = 11,700, Mw = 17,500, PDI = 1.50.

3. Results and discussion

3.1. Polymerization

The synthetic routes for monomers M1, M2, M3 and M4 can be found in Scheme S1 in supporting information. The synthetic routes of the copolymers are shown in Scheme 1. Alternating copolymer P1 was prepared by Suzuki-Miyaura cross-coupling reaction using equimolar amounts of the comonomers such as M1 and M3 in the presence of Pd (PPh₃)₄ in a mixture of toluene and aqueous K_2CO_3 . A similar procedure was used as that described for P1 by the synthesis of random copolymers **P2** and **P3** using monomers **M1**, **M3**, **M2** and **M1**, **M3**, **M4**, respectively. The crude polymer was further purified by a Soxhlet extraction in methanol and acetone for 24 h to remove catalyst, by-product and oligomers before fully solubilizing in hot dichloromethane.

The molecular weights of the polymers **P1**, **P2** and **P3** were determined by gel permeation chromatography (GPC) in THF solution, calibrated against narrow polydispersity index polystyrene standards, using refractive index (RI) detection. The results of the number average, weight average molecular weights, polydispersity index (PDI) and reaction yields were summarized in Table 1. The measured number average molecular weight (*M*n) of the copolymers **P1**, **P2** and **P3** was 20,800, 8000 and 11,700 g/mol and the PDI was 1.93, 1.33 and 1.50, respectively. The higher *M*n value of 20,800 g/mol for polymer **P1** compared to that of **P2** (8000 g/mol) and **P3** (11,700 g/mol) can be possibly attributed to the better solubility of the resulting polymers. In addition, the reaction yield of **P1**, **P2** and **P3** is 60, 47 and 43%, respectively.

3.2. Characterization of polymers by NMR spectroscopy

The ¹H NMR spectra of **P1**, **P2** and **P3** are shown in Fig. 1. The ¹H NMR spectrum of P1 recorded in CDCl₃ shows a doublet at 7.74 ppm corresponding to the hydrogens of fluorene rings meta to the carbon bonded to two triethylene glycol monomethyl ether (TEG) chains. The signals between 7.65 and 7.60 ppm are assigned to the hydrogens of the fluorene rings ortho and para to the carbon bonded to two TEG chains and to the hydrogens of phenyl rings bonded to the carbons meta to the nitrogen. The hydrogens of phenyl rings bonded to the carbons ortho to the nitrogen appear at 7.17 ppm. The signals between 3.50 and 2.40 ppm integrating to 30 hydrogens are associated with the hydrogens of the triethylene glycol chains. A broad signal at the 3.87 ppm indicates alpha hydrogens of the octyl group attached on the nitrogen. The signals below 2.00 ppm correspond to the remaining hydrogens of the octyl chain. A broad peak at 7.74 ppm for P2 is associated to the hydrogens of fluorene rings meta to the carbon bonded to two triethylene glycol monomethyl ether chains. A signal appears at 7.65–7.59 ppm corresponds to the hydrogens of the fluorene rings ortho and para to the carbon bonded to two TEG chains and to the hydrogens of phenyl rings attached to the carbons meta to the nitrogen. In addition, the hydrogens of the aromatic rings of diphenylamine bonded to the carbons ortho to the nitrogen were found at 7.10 ppm. The signals below 4.00 ppm are attributed to the TEG and octyl chain hydrogens. The ¹H NMR spectrum of **P3** observed a broad signal at 7.80 ppm is associated to the hydrogens of the fluorene rings meta to the carbon bonded to two TEG chains. Signals appear at 7.65-7.59 ppm correspond to the hydrogens of the fluorene rings ortho and para to the carbon bonded to two TEG chains and to the hydrogens of phenyl rings attached to the carbons meta to the nitrogens. In addition, signals between 7.20 and 7.05 ppm correspond to the hydrogens of the aromatic rings of diphenylamine bonded to the carbons ortho to the nitrogens. Again, the signals below 4.00 ppm are attributed to the hydrogens of the TEG and octyl chains. The signals associated with the hydrogens of the corresponding polymers are fully characterized. The results of ¹H NMR spectra of all polymers confirmed the microstructure of the polymer backbone. In addition, the position of peaks corresponded to the hydrogens were confirmed by 2D ¹H-¹H COSY spectra in the Figure S1-S3 in supporting information. The mole percent of each monomer unit can be calculated and the microstructures of the copolymers can be evaluated from the integration areas of the corresponding peaks from the ¹H NMR spectra of the copolymers.

3.3. Conjugated polymer nanoparticles and aggregates

Conjugated polymer nanoparticles were prepared by rapid precipitation method. A polymer solution in THF (1 mg/mL) was rapidly injected into water with the relative amount of polymer solution and



Scheme 1. Synthetic routes to conjugated copolymers P1, P2 and P3 (R₁ = -CH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃, R₂ = -octyl).

Table 1
The number average, weight average molecular weights, polydispersity index
and reaction yields of polymers P1-P3.

Polymer	Reaction Condition	Mn (g/mol) ^a	Mw (g/mol) ^a	PDI ^a	Yield (%) ^b	
P1	Toluene, 110 °C, 56 h	20,800	40,200	1.93	60	
P2	Toluene, 110 °C, 56 h	8000	10,600	1.33	47	
P3	Toluene, 110 °C, 56 h	11,700	17,500	1.50	43	

^a Determined by GPC in THF solution calibrated with monodisperse polystyrene standards using RI detection.

^b After Soxhlet extraction.

non-solvent (water) in a volume ratio of 1: 4 for each experiment with vigorous stirring at room temperature. Residual THF was removed from the resultant nanoparticle suspensions by blowing argon over the suspension. Self-assembled polymeric aggregates were prepared by dissolving 2 mg of polymers into 2 mL of THF. The vial containing a polymer solution was then placed in a 50 mL vial containing 5 mL of a nonsolvent such as acetone or methanol and the outer vial was capped. The nonsolvent vapors gradually diffused into the solution of the polymers to give a suspension after 4 days at room temperature. Scanning electron microscopy (SEM) images were taken from air-dried suspension of polymers drop-cast onto the glass slide (Fig. 2). Conjugated polymer P1 from THF/MeOH mixture afforded regular sheetlike features (Fig. 2a) possibly due to slow nucleation of polymer backbones in the THF/MeOH system. The SEM image of the conjugated polymer P1 from the mixture of THF/acetone showed nanoaggregates instead of well-dispersion structures (Fig. 2b). In addition, the SEM image of the conjugated polymer nanoparticles P1 from the dispersion method in water showed mainly a spherical geometry (Fig. 2c). The SEM images of the conjugated polymer P2 from THF/MeOH mixture exhibited regular sheet-like features (Fig. 2d). A clear spherical geometry was observed for P2 from a solvent combination of THF/acetone (Fig. 2e). Conjugated polymer nanoparticle P2 formed by the dispersion method in water was not as smooth as the spheres of P1 due to the formation of partial aggregates (Fig. 2f). An irregular aggregate structure (Fig. 2g) was observed for the P3 from the THF/MeOH mixture. Spherical assemblies were formed upon the diffusion of acetone into the polymer solution of P2 (Fig. 2h) with a relatively high content of diphenylamine moieties. In addition, irregular aggregates (Fig. 2i) were observed for P3 dispersed in water. The relatively high contents of TEG or octyl substituted diphenylamine moieties of P2 and P3 disturbed the planarity of polymer backbones to form twisted configurations, leading to disordered inter-chain packing which contributed to a spherical morphology [46-48]. The polymers with a relatively high content of diphenylamine moieties possibly aggregate due to low affinity for the nonsolvents which minimizes the contact area with the hydrophobic polymer, and contributes to the gradual growth of a spherical geometry [49]. Both the average size and the morphology of the polymers were strongly depended on the solubility of the polymers in a good solvent as well as the rate of diffusion of the poor solvent.



Fig. 1. H¹ NMR spectra of polymers (a) P1, (b) P2 and (c) P3 in CDCl₃.

As shown in Fig. 2, the well-defined spherical structure and uniform particle distribution of the copolymers **P1** prepared from rapid precipitation in water can be observed. The average hydrodynamic diameter of copolymers **P1-P3** dispersed in water determined by dynamic light scattering (DLS) measurement is shown in Fig. 3. A range of 75–90 nm (Fig. 3a) for the rapidly precipitated copolymer **P1** was measured, which is in agreement with the particle size calculated by FE-SEM images of the copolymer **P1**. The average hydrodynamic diameter of rapidly precipitated copolymer **P2** (Fig. 3b) and **P3** (Fig. 3c) is 421 and 350 nm, respectively which is relatively large compared to that of



Fig. 2. SEM images of P1 from (a) THF/MeOH, (b) THF/acetone and (c) water dispersion, P2 from (d) THF/MeOH (e) THF/acetone and (f) water dispersion and P3 from (g) THF/MeOH (h) THF/acetone and (i) water dispersion.



Fig. 3. Histograms of size distribution of the polymers (a) P1 (b) P2 and (c) P3 dispersed in water obtained by DLS analysis.



Fig. 4. XRD patterns of cast films of (a) P1, (b) P2 and (c) P3 from THF/MeOH, THF/acetone, water dispersion and powder.

P1 possibly due to the nature of the aggregate features of copolymers **P2** and **P3**. The highly hydrophobic nature of random copolymers **P2** and **P3** containing a relatively large content of hydrophobic moieties unable to precipitate rather than forming aggregates in aqueous media.

X-ray diffraction (XRD) is one of the most utilized techniques to confirm the differences in the crystallinity of copolymers. As shown in the Fig. 4, the XRD of the blank sample did not show any diffraction peaks as we expected. The self-assembled copolymers with a combination of solvents, such as THF/MeOH and THF/acetone were crystallized and the XRD 2theta peaks were around 6° and 10°. It is worth noting that a relatively strong peak intensity was observed for P2 prepared from the THF/acetone mixture compared to that of P1 and P3 possibly due to the a reorientation of the octyl chain taking place at the interface between THF and acetone. The neat polymer powders and

Table 2

Photophysical properties of P1-P3.

Polymer	λ_{abs}^{a} (nm)	$\lambda_{abs}^{\ \ b}$ (nm)	λ_{abs}^{c} (nm)	λ_{PL}^{a} (nm)	λ_{PL}^{b} (nm)	λ_{PL}^{c} (nm)	$\Phi_{\mathrm{PL}}{}^{\mathrm{d}}$ (%)	$\Phi_{\mathrm{PL}}{}^{\mathrm{e}}$ (%)	$\Phi_{\mathrm{PL}}{}^{\mathrm{f}}$ (%)	$\Phi_{\mathrm{PL}}{}^{\mathrm{g}}$ (%)
P1	385	397	383	436	444	440	55	0.59	42	30
P2	375	381	420	440	443	438	30	0.33	22	19
P3	376	386	417	440	440	438	28	0.25	20	15

 $^{\rm a}\,$ In dilute THF solution (5 \times 10 $^{-6}\,$ M).

^b Polymer thin films spin-coated from a polymer THF solution.

^c Polymer nanoparticle dispersion from THF/water mixture.

^d Quantum yields from polymer solution.

^e Quantum yields from polymer dispersed in water.

^f Quantum yields of self-assembled polymers from THF/MeOH and.

^g Quantum yields of self-assembled polymers from THF/acetone.



Fig. 5. Normalized absorption (solid lines) and fluorescence (dashed line) spectra of P1-P3; (a) conjugated polymer solution (in THF), (b) solid state and (c) water dispersion.

polymer nanoparticles prepared by rapid precipitation for **P1**, **P2** and **P3** do not show any diffraction peaks indicating the amorphous nature of the polymers.

3.4. Photophysical properties of the copolymers

The details of photophysical properties of the conjugated polymer in solutions, in solid state, as well as rapid precipitation and self-assembly from THF/MeOH and THF/acetone are shown in Table 2 and Table S1. The absorption and fluorescence spectra of P1-P3 in solution, in solid state and in water dispersion are shown in Fig. 5. The conjugated polymer P1 containing an alternating fluorene-diphenylamine structure with a relatively high molecular weight exhibits a longer absorption wavelength (385 nm) in THF solution compared to that of P2 (375 nm) and P3 (376 nm). The solid state absorption maximum of the polymers for P1, P2 and P3 is at 397, 381 and 386 nm, respectively which is more red-shifted compared to that of solution possibly due to the aggregation formation. The dense aggregation characteristics of rapid precipitation for polymers P2 and P3 show a red shifted absorption maxima compared to the solution and the solid state [50,51]. However, the absorption maximum of conjugated polymer nanoparticles for P1 was blue shifted with a longer wavelength tail compared to the solution and the solid state. This phenomenon can be attributed to the densely packed structure of the particles causing a decrease in the conjugation length of the polymer backbones due to a high degree of bending [52].

The solution photoluminescence emission maximum of polymers **P1-P3** was 436, 440 and 440 nm, respectively. The large stokes shift for **P2** (65 nm) and **P3** (64 nm) compared to **P1** (51 nm) suggests a more planar structure in the excited state due to redistribution of the electron density in the excited state [53]. The solid state emission maximum of polymers **P1-P3** was 444, 443 and 440 nm, respectively which is redshifted compared to that of solution. This could be attributed to aggregation in solid state. In comparison to the solution, the emission maximum of the polymer nanoparticles for **P2** and **P3** was blue shifted by 2 nm and the polymer nanoparticles for **P1** was red shifted by 4 nm. The red-shift in the emission maximum for the polymer nanoparticles of

P1 is mainly caused by the aggregation of conjugated polymer upon nanoparticle formation which increases the interactions between segments of the polymer chains [54]. The fluorescence quantum yields of polymer nanoparticles were significantly quenched compared to that of the solution (0.59%, 0.33% and 0.25% in aqueous media versus 55%, 30% and 28% for P1, P2 and P3 in THF, respectively). The nature of aggregation of polymer chains (interchain interactions) in the aqueous media and self-aggregation driven by the poor solubility as well as π - π interactions quenched the fluorescence [55]. The nature of conjugated polymer backbone influenced spectroscopic properties, such as absorption and emission efficiency, as consequence of the internal organization of aggregation. A higher percentage of a hydrophobic segment in the polymer chain will have stronger hydrophobic-hydrophobic interactions between polymer chains, which quench the emission intensity in aqueous media. However, the fluorescence quantum yields of polymers P1-P3 from THF/MeOH or THF/acetone were much higher compared to that of the polymers prepared by rapid precipitation. The absorption and photoluminescence maximum of self-assembled aggregates (Figure S4 and Table S1) is slightly red shifted in a range of 1–2 nm in comparison to solution. The smaller $\Delta\lambda$ max values between polymer solution and self-assembled aggregates compared with polymer nanoparticles derived from rapid precipitation imply that the interchain interactions of self-assembled aggregates are relatively weak.

4. Conclusion

In summary, π -conjugated copolymers containing fluorene and diphenylamine with alkyl and TEG side chains have been prepared by Suzuki-Miyaura cross-coupling reaction and their structures were fully characterized. The shapes and structures of the polymers were highly depended on the planarity of π -conjugated system, the molecular weights and the solvent combination. These factors influenced the internal organization of aggregation and the interactions between copolymers and surrounding media. Such parameters are powerful components for determining morphologies and optical properties and are useful tools for developing strategies for converting π -conjugated

polymers into colloidal architectures. Self-assembled polymers with micrometer sized particles from the solvent diffusion method exhibited a relatively high photoluminescence quantum yield in comparison with that of the conjugated polymer nanoparticles formed from the rapid precipitation method.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2018.12.039.

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