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Synthesis of Comb Copolymers with Pendant Chromophore Groups Based on RAFT Polymerization and Click Chemistry and Formation of Electron Donor−Acceptor Supramolecules

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ABSTRACT: Comb copolymers comprising hydrophilic poly(ethylene glycol) comb chains and hydrophobic fluorescent pyrenyl groups were synthesized by a combination of reversible addition−fragmentation chain transfer polymerization and click chemistry. FTIR, ^{1}H NMR, and gel permeation chromatograph results indicated successful synthesis of the comb copolymers with well-defined structures. The self-assembly of comb copolymers in aqueous solution was investigated. The comb copolymers with different compositions were able to self-assemble into micellar structure or vesicle structure. The pendant pyrenyl groups on the comb copolymer chains had electron donor−acceptor (EDA) interaction with 4-bromo-*N,N′*-dimethylaniline (BDMA). Vesicle structure formed by BDMA and comb copolymer via EDA interaction was observed by transmission electron microscopy. The fluorescence properties of the supramolecular structure were studied in detail.

Introduction

To establish architecture−property relationships and to study self-assembly properties either at solid state or in solutions, polymers with different topological structures, for example, linear block, gradient graft, comb-shaped, star-shaped, hyperbranched, and dendritic copolymers, have been synthesized.[1,2] In the past decade, controlled/living radical polymerization (C/LRP) techniques have been used widely in the preparation of (co)polymers with different architectures, predetermined molecular weights, and low molecular weight polydispersities.[3] Despite the versatility of C/LRP techniques, it is still a challenge to find feasible means to introduce functional groups onto polymer chains. These functional polymers, for example, fluorescent groups labeled polymers, biofunctionalized polymers, and drug containing polymers, can find wide applications in chemistry, materials science, and biomedical science fields.[4−7] However, because of the possible side reactions and low concentration of functional groups, highly efficient and controllable reactions are required. Click chemistry is attractive because of the moderate reaction conditions conducted in multiple solvents, tolerance to numerous functional groups, high yields, and little or no side reactions.[8−10] Therefore, click chemistry is particularly important in chemical synthesis in which high conversion of functional groups is desired. The combination of C/LRP and click chemistry is an efficient way to prepare functional polymeric materials. Some research groups have reported the synthesis of polymers based on atom transfer radical polymerization or nitroxide-mediated polymerization and subsequent azide−alkyne coupling reactions.[11−15] Among the C/LRP techniques reported to date, reversible addition−fragmentation chain transfer (RAFT) polymerization is one of the most versatile techniques due to the facile experimental setup and great potential for scale-up reactions.[16,17] Taking advantage of the flexibility of RAFT polymerization and the efficiency and specificity of click chemistry, a variety of functional polymers were prepared.[18−27]

Because of the importance in various physical, chemical, and biological processes, electron donor−acceptor (EDA) interactions between organic molecular donor and acceptor have been extensively studied.[28−33] The previous studies focused on EDA interactions between small molecules,[28,29] in solid films,[34−36] and in supramolecular structures.[37−40] However, the role of EDA interactions in the self-assembly structures of macromolecules still remains unknown.

It is difficult to conduct homopolymerization of the monomers with chromophore groups by free radical polymerization due to the steric hindrance of the chromophore groups and the low solubility of the polymers in ordinarily solvents.[41] It is necessary to find a new way to prepare functional polymers with chromophore groups. Herein we report the preparation of comb copolymers with hydrophilic poly(ethylene glycol) comb chains and pendant chromophore groups based on RAFT polymerization and click coupling reaction (Scheme 1). Because of well-known photochemical properties and the electron or energy transfer abilities, pyrenyl groups were chosen to be introduced onto polymer chains. The grafting of the pyrenyl groups was carried out by copper-mediated cycloaddition [3 + 2] of azido pyrene onto main chain with pendent acetylene groups. Besides synthesis of the comb copolymers, we are also interested in the relationship between polymer structure and fluorescent properties and the role of EDA interactions in the self-assembly of macromolecules.

Experimental Section

Materials. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, Aldrich, $M_n = 475$) was purified by passing the THF solution of PEGMA through a basic aluminum oxide column and removing THF under reduced pressure. CuBr (Sinopharm Chemical Reagent Co., 99.5%) was purified by washing with glacial acetic acid.[42] 4,4′-Azobis(4-cyanopentanoic acid) (ABCPA, Aldrich, 97%) was recrystallized from methanol and dried under vacuum at room temperature. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%), 1-pyrenemethanol (98%), sodium azide (NaN_3, 99%), propargyl alcohol (PgOH, 99%), 2-bromoisobutyl bromide (98%), *N*-ethyl-*N′*-(3-(dimethylamino)propyl)carbodiimide (EDC, 97%), 4-(dimethylamino)pyridine (DMAP, 99%), and 4-bromo-*N,N′*-dimethylaniline (BDMA, 97%) were purchased from Aldrich and used as received. Chain transfer agent (CTA) (4-cyanopentanoic acid) dithiobenzoate (CPADB) was prepared by using a method

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Scheme 1. Schematic Illustration of a General Approach to the Preparation of Comb Copolymers with Pendant Pyrenyl Groups Based on "Click Chemistry"

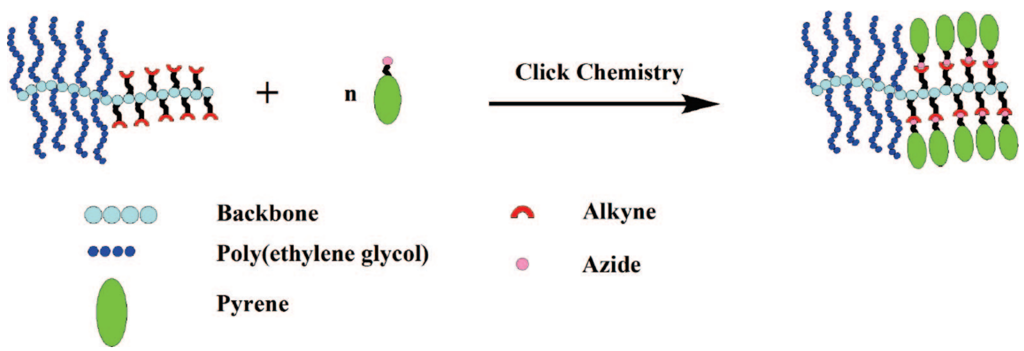


Table 1. Summary of Molecular Weights and Molecular Weight Distributions of Macromolecular Chain Transfer Agent Poly(poly(ethylene glycol) methacrylate) (PPEGMA),[a,b] Poly(poly(ethylene glycol) methacrylate)-*block*-poly(propargyl methacrylate) PPEGMA$_m$-*b*-PPgMA$_n$ Comb Copolymer,[c] and Pyrene-Bearing Block Copolymer PPEGMA$_m$-*b*-PPyMA$_n$ Prepared by Click Reaction between Pyrenyl-N$_3$ and PPEGMA$_m$-*b*-PPgMA$_n$[d]

sample	CTA	temp (°C)	M_n (× 10^{-3} g mol^{-1})	PDI
PPEGMA$_{13}$ [e]	CPADB	60	6.71[e]	1.14
PPEGMA$_{13}$-*b*-PPgMA$_6$[f]	PPEGMA$_{13}$	60	7.71[e]/7.50[f]	1.17
PPEGMA$_{13}$-*b*-PPyMA$_6$	−	rt	9.10[e]/9.50[f]	1.21
PPEGMA$_{13}$-*b*-PPgMA$_{24}$[f]	PPEGMA$_{13}$	60	12.10[e]/9.70[f]	1.35
PPEGMA$_{13}$-*b*-PPyMA$_{24}$	−	rt	15.16[e]/15.80[f]	1.23
a-alkyne-PPEGMA$_7$[e]	PCPADB	60	4.69[e]/3.60[f]	1.11
a-alkyne-PPEGMA$_7$-*b*-PPgMA$_3$[f]	*a*-alkyne-PPEGMA	60	5.26[e]/4.10[f]	1.22
a-pyrenyl-PPEGMA$_7$-*b*-PPyMA$_3$	−	rt	5.45[e]/5.50[f]	1.23

[a] The initiator used in all the reversible addition−fragmentation chain transfer (RAFT) polymerizations is 4,4′-azobis(4-cyanopentanoic acid) (ABCPA). [b] Conditions: RAFT polymerizations using (4-cyanopentanoic acid) dithiobenzoate (CPADB) as the chain transfer agent (CTA): [PEGMA]:[CPADB]:[ABCPA] = 60:4:1; RAFT polymerizations using (propargyl 4-cyanopentanate) dithiobenzoate (PCPADB) as CTA: [PEGMA]:[PCPADB]:[ABCPA] = 48:4:1. [c] Conditions: RAFT polymerizations using PPEGMA$_{13}$ as macro-CTA: [PgMA]:[PPEGMA$_{13}$]:[ABCPA] = 75:5:1. RAFT polymerizations using *a*-alkyne-PPEGMA$_7$ as macro-CTA: [PgMA]:[*a*-alkyne-PPEGMA$_7$]:[ABCPA] = 60:4:1. [d] Conditions: click coupling reactions in DMF: [alkyne]:[pyrene-N$_3$]:[CuBr]:[PMDETA] = 1:1.2:1:1. [e] Determined by gel permeation chromatograph based on polystyrene standards. [f] Determined by ^{1}H NMR results.

similar to previous literature.[43−45] Propargyl methacrylate (PgMA) monomer was prepared by a reaction of PgOH with methacryloyl chloride in the presence of triethylamine. The CTA (propargyl 4-cyanopentanate) dithiobenzoate (PCPADB) was synthesized by esterfication of PgOH with CPADB (details can be found in the Supporting Information). All the polymerizations were performed in Schlenk flasks under nitrogen. All the solvents were distilled before use.

Synthesis of Pyrene-Br. 1-Pyrenemethanol (1.0 g, 4.3 mmol) was added to a solution of triethylamine (0.90 mL, 6.5 mmol) in 15 mL of anhydrous THF, and 2-bromoisobutyl bromide (0.82 mL, 6.5 mmol) was added dropwise under stirring at 0 °C. The reaction was conducted at room temperature overnight. After the reaction, the precipitate was filtered and the solution was washed with HCl solution (1 mol/L), NaOH solution (1 mol/L), and water. The organic layer was dried over MgSO$_4$ and filtered. The crude product was purified by column chromatography (hexane:ethyl acetate, 10:1), and pyrenyl-Br was obtained (yield: 90%). MS (*m*/*e*): 404 (M + Na$^+$). ^{1}H NMR (CDCl$_3$), δ ppm: 7.99−8.19 (aromatic H, 9H,), 5.92 (C**H**$_2$O, 2H), 1.92 (C**H**$_3$, 6H). ^{1}H NMR spectrum of pyrenyl-Br is shown in Figure S1a. The resonance peak at 1.92 ppm was attributed to the protons on two methyl groups ((C**H**$_3$)$_2$CBr), which confirmed the successful synthesis of pyrenyl-Br.

Synthesis of Pyrenyl Azide (Pyrenyl-N$_3$). Pyrenyl-Br (0.50 g, 1.3 mmol) and NaN$_3$ (0.11 g, 1.6 mmol) were dissolved in 5 mL of DMF and stirred overnight at room temperature, and the product pyrenyl-N$_3$ was recovered by filtration. The resonance peak at 1.92 ppm (peak **H**$_c$ in Figure S1a) disappears completely, and a new peak at 1.46 ppm typical for the (C**H**$_3$)$_2$C−N$_3$ protons can be observed (**H**$_{c'}$ in Figure S1b). The yield is about 95%.

RAFT Polymerization of PEGMA. A typical polymerization was described as follows. PEGMA (2.0 mL, 4.6 mmol), ABCPA (5.8 mg, 0.020 mmol), and chain transfer agent CPADB (46.3 mg, 0.17 mmol) were dissolved in 2 mL of DMF in a 10 mL Schlenk flask. The solution was degassed by three freeze−pump−thaw cycles. The polymerization was conducted at 60 °C for 16 h. The polymerization was stopped by quenching the Schlenk flask in ice water. After being concentrated, the polymer was precipitated in cold diethyl ether, and poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA) with a characteristic pink color was obtained. The viscous polymer was dried under vacuum. The monomer conversion determined by gravimetry is 34%. The poly(poly(ethylene glycol) methyl ether methacrylate) prepared by using PCPADB as chain transfer agent was denominated as *a*-alkyne-PPEGMA$_7$. The molecular weights and molecular weight distributions were determined by GPC (Table 1).

Synthesis of Poly(poly(ethylene glycol) methacrylate)-*block*-poly(propargyl methacrylate) (PPEGMA$_m$-*b*-PPgMA$_n$). PgMA (0.10 g, 0.81 mmol), macromolecular chain transfer agent (macro-CTA) PPEGMA (0.30 g, 0.075 mmol), and ABCPA (4.2 mg, 0.015 mmol) were dissolved in 3 mL of DMF in a Schlenk flask. The solution was degassed by three freeze−pump−thaw cycles and was stirred at 60 °C for 8 h. The reaction was stopped by quenching the Schlenk flask in ice water. The crude polymer was analyzed by ^{1}H NMR to determine the PgMA monomer conversion (Figure S5). The comb copolymer prepared by using *a*-alkyne-PPEGMA$_7$ as macromolecular chain transfer agent was denominated as *a*-alkyne-PPEGMA$_7$-*b*-PPgMA$_3$.

Synthesis of Pyrene-Bearing Comb Copolymers PPEGMA$_m$-*b*-PPyMA$_n$ through Huisgen's 1,3-Dipolar Cycloadditions. Click reactions between akylyne groups on PPEGMA$_m$-*b*-PPgMA$_n$ and pyrenyl-N$_3$ were performed in DMF. A typical reaction was described as follows. PEGMA$_m$-*b*-PgMA$_n$ (0.15 g), PMDETA (35.3 μL, 0.014 mmol), and pyrenyl-N$_3$ (0.029 g, 0.084 mmol) were dissolved in 3 mL of anhydrous DMF and were degassed by three freeze−pump−thaw cycles. Upon addition of CuBr (0.002 g, 0.014 mmol) the solution turned brown. After stirring for 24 h, the solution was passed through a neutral Al$_2$O$_3$ column to remove the copper complex, and then the concentrated crude product was precipitated in diethyl ether. The final product was dried under vacuum.

Characterization. ^{1}H NMR measurements were performed on a Varian UNITY-plus 400 M nuclear magnetic resonance spectrometer (field strength, 9.4 T) using $CDCl_3$ (Cambridge Isotope, D 99.8% + TMS 0.03%, CIL) as the solvent at room temperature. Infrared spectra were obtained on a Bio-Rad FTS 6000 system using diffuse reflectance sampling accessories. The apparent molecular weights and molecular weight distributions of the polymers were determined at 35 °C on a gel permeation chromatograph (GPC) equipped with a Waters 717 autosampler, Waters 1525 HPLC pump, three Waters UltraStyragel columns with 5K−600K, 500−30K, and 100−10K molecular ranges, and a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. Polymer solution (150 μL) was injected through Waters Styragel column. The number-average molecular weights (M_n) and molecular weight distributions of the polymers were calibrated on polystyrene standards. Ultraviolet−visible absorption spectra were recorded at 25 °C on a Cary 300 UV spectrophotometer using a quartz cell of 1 cm path length. The samples were scanned in the range of 800−200 nm. The scanning speed was set at 200 nm/min. Steady-state fluorescence spectra were recorded on a Varian Cary eclipse fluorescence spectrophotometer (Varian Instruments, Palo Alto, CA). The excitation slits and emission slits were set at 5 nm. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 20 S-TWIN electron microscope equipped with a Model 794 CCD camera (512 × 512) at an operating voltage of 200 kV. The TEM specimens were prepared by depositing aqueous solutions on Foemvar grids; water was evaporated in air. Before measurements the specimens were stained by RuO_4.

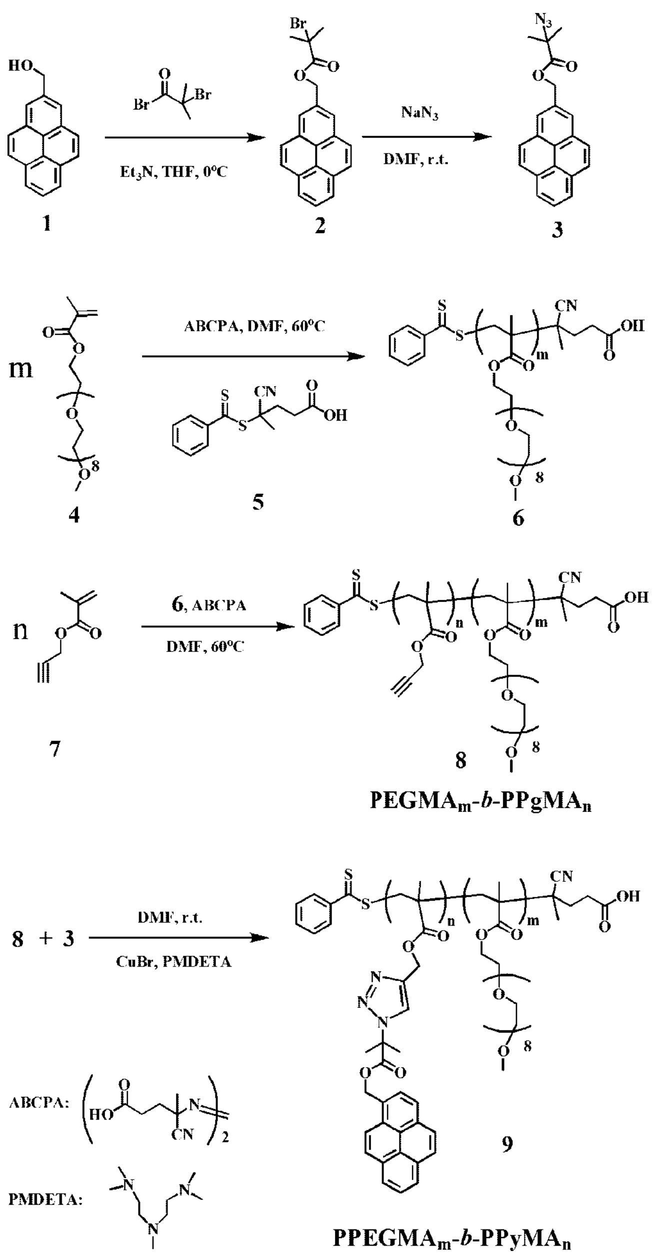
Results and Discussion

As shown in Scheme 2, the preparation of PPEGMA$_m$-*b*-PPyMA$_n$ comb copolymers **9** is based on three-step synthetic strategy: (1) synthesis of pyrenyl-Br (**2**), pyrenyl azide (pyrenyl-N_3) (**3**), and macro-CTA PPEGMA (**6**) by RAFT polymerization of PEGMA (**4**); (2) synthesis of acetylene-functionalized PPEGMA$_m$-*b*-PPgMA$_n$ (**8**) by RAFT polymerization of PgMA; (3) click coupling reaction of precursors containing antagonist functionalities. In this paper the comb copolymers bearing pendant acetylene groups and pyrenyl groups were assigned as PPEGMA$_m$-*b*-PPgMA$_n$ and PPEGMA$_m$-*b*-PPyMA$_n$, where *m*, *n* indicate the repeating unit numbers of the respective blocks.

As shown in Scheme 2, pyrenyl-Br (**2**) was synthesized by a reaction of 1-pyrenemethanol and 2-bromoisobutyl bromide in anhydrous THF solution with triethylamine. Pyrenyl-Br (**2**) was reacted with 1.2 equiv of sodium azide in DMF at room temperature overnight. The ^{1}H NMR result confirms that the conversion of the bromide to azide is quantitative (Supporting Information).

RAFT polymerization of PEGMA was conducted at 60 °C in DMF for 16 h. By employing macro-CTA PPEGMA (**6**), PgMA was polymerized at 60 °C in DMF to yield PPEGMA$_m$-*b*-PPgMA$_n$ (**8**) (Scheme 2). The copolymers were precipitated in ether and dried under vacuum. The macro-CTA PPEGMA and PPEGMA$_m$-*b*-PPgMA$_n$ were analyzed by ^{1}H NMR (spectra a and b in Figure 1). For PPEGMA a signal at 4.06 ppm corresponding to the oxymethylene protons $-O-CH_2-(H_a)$ could be detected; for PPEGMA$_m$-*b*-PPgMA$_n$ not only the signal at 4.06 ppm but also a signal at 4.62 ppm due to the methylene protons on the ester groups of PgMA (**H**$_b$) could be observed. GPC analysis demonstrated high CTA efficiency and well-controlled polymerization (Figure 2). In the curve, the appearance of a small shoulder at high molecular region might indicate some termination reactions which usually occur when two growing macroradicals combine together instead of undergoing the transfer to the RAFT agent[46] or reaction between the alkyne groups of PgMA monomer and radicals during the polymerization.[47] The molecular weights and molecular weight distributions of the polymers are summarized in Table 1. The molecular weights were close to the theoretical values calculated according to the monomer conversions. For the PPEGMA macro-CTA prepared by using PCPADB as a CTA, there is an acetylene group at the end of the polymer chain, which could be used for further click coupling. In order to avoid the steric hindrance and guarantee high grafting efficiency of pyrenyl groups, the degrees of polymerization of the PgMA blocks were controlled at low levels.

Scheme 2. Synthesis of Comb Copolymers with Hydrophilic Poly(ethylene glycol) Comb Chains and Pendant Pyrenyl Groups Based on Reversible Addition−Fragmentation Chain Transfer Polymerization and Click Chemistry[a]



[a] THF and DMF represent tetrahydrofuran and *N*,*N*-dimethylformamide, respectively.

Pyrenyl groups were grafted onto polymer chains by click coupling reactions between pyrenyl-N_3 (**3**) and PPEGMA$_m$-*b*-PPgMA$_n$ (**8**) (Scheme 2). The coupling reactions catalyzed by the CuBr/PMDETA complex were conveniently performed in DMF solution at room temperature. After 24 h of reaction the targeted PPEGMA$_m$-*b*-PPyMA$_n$ comb copolymers were obtained (Scheme 2). A slight excess pyrenyl-N_3 was used (1.2 equiv) in order to drive the coupling reactions to completion. The excess pyrenyl-N_3 was removed by precipitation of the polymer

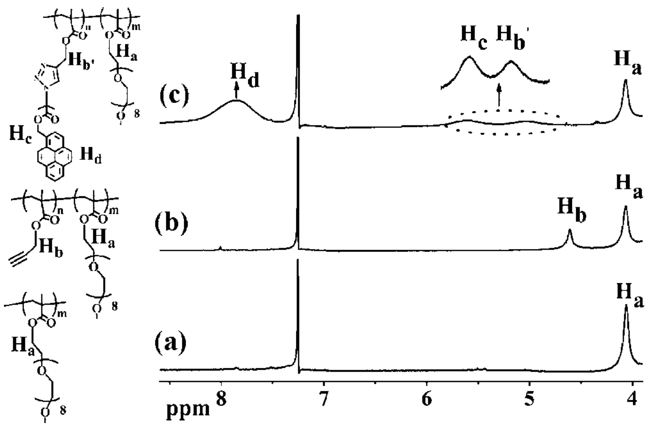


Figure 1. ^{1}H NMR spectra (zooms of the regions 8.6−3.9 ppm) and peak labels for (a) poly(poly(ethylene glycol) methacrylate) (PPEGMA$_{13}$) macromolecular chain transfer agent, (b) block copolymer of PEGMA and propargyl methacrylate (PPEGMA$_{13}$-*b*-PPgMA$_6$), and (c) pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_6$ prepared by click reaction between pyrenyl azide (pyrenyl-N$_3$) and PPEGMA$_{13}$-*b*-PPgMA$_6$. All spectra were recorded at room temperature in CDCl$_3$.

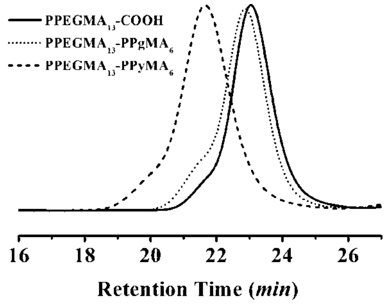


Figure 2. Gel permeation chromatograph curves for macromolecular chain transfer agent poly(poly(ethylene glycol) methacrylate) (PPEGMA$_{13}$-COOH), poly(poly(ethylene glycol) methacrylate)-*block*-poly(propargyl methacrylate) (PPEGMA$_{13}$-*b*-PPgMA$_6$) comb copolymer, and pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_6$ prepared by click reaction between pyrenyl azide (pyrenyl-N$_3$) and PPEGMA$_{13}$-*b*-PPgMA$_6$.

in diethyl ether, and the pure polymer was obtained. In this paper three comb copolymers *a*-pyrenyl-PPEGMA$_7$-*b*-PPyMA$_3$, PPEGMA$_{13}$-*b*-PPyMA$_6$, and PPEGMA$_{13}$-*b*-PPyMA$_{24}$ were prepared. GPC traces showed clear shifts toward higher molecular weight region after click reaction (Figure 2). Comparing with the starting polymer PPEGMA$_{13}$-*b*-PPgMA$_6$, the molecular weight of PPEGMA$_{13}$-*b*-PPyMA$_6$ increased from 7.7K to 9.1K after click reaction (Table 1). The reaction was also monitored by ^{1}H NMR spectroscopy (spectrum c in Figure 1). The disappearance of the signal of methylene protons adjacent to the acetylene group ($CHCC\mathbf{H_2}$−) at 4.61 ppm and the appearance of the new signal of methylene protons adjacent to the triazole ring at 5.13 ppm (R−$\mathbf{CH_2}$−triazole−) were observed (Figure 1). The 1,3-dipolar cycloaddition coupling reaction was also supported by FTIR spectra. Figure 3 shows FTIR spectra of PPEGMA, PPEGMA$_{13}$-*b*-PPgMA$_6$, and PPEGMA$_{13}$-*b*-PPyMA$_6$. The absorption peak at 3248 cm^{-1} on spectrum b is attributed to the vibration of carbon−carbon triple bond. However, after click reaction the peak at 3248 cm^{-1} disappeared and new absorption peaks at 1600 and 3140 cm^{-1}, characteristics of the vibrations of the triazole unsaturations and carbon−hydrogen on pyrenyl groups could be observed (spectrum c in Figure 3).

One comb copolymer chain is composed of one hydrophilic PPEGMA comb block and one hydrophobic PPyMA block, which makes it possible for the copolymers to self-assemble into a variety of structures in aqueous solution. In the following part of this paper we study self-assembly of the comb copolymers and supramolecular structure formed by BDMA small molecules and comb copolymer chains in aqueous solution.

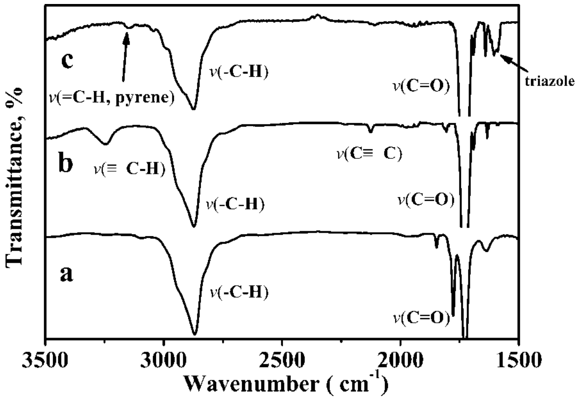


Figure 3. FTIR spectra of (a) macromolecular chain transfer agent poly(poly(ethylene glycol) methacrylate) (PPEGMA), (b) poly(poly(ethylene glycol) methacrylate)-*block*-poly(propargyl methacrylate) (PPEGMA$_{13}$-*b*-PPgMA$_6$) comb copolymer, and (c) pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_6$ prepared by click reaction between pyrenyl azide (pyrenyl-N$_3$) and PPEGMA$_{13}$-*b*-PPgMA$_6$.

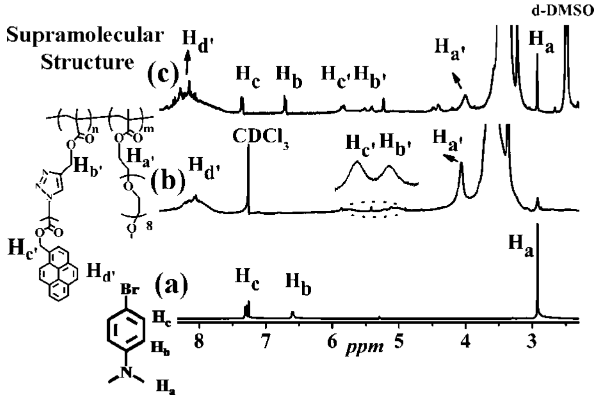


Figure 4. ^{1}H NMR spectra of (a) 4-bromo-*N*,*N'*-dimethylaniline (BDMA), (b) pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_{24}$ prepared by click reaction between pyrenyl-azide (pyrenyl-N$_3$) and poly(poly(ethylene glycol) methacrylate)-*block*-poly(propargyl methacrylate) (PPEGMA$_{13}$-*b*-PPgMA$_{24}$) comb copolymer, and (c) supramolecular structure formed by PPEGMA$_{13}$-*b*-PPyMA$_{24}$ and BDMA. Spectrum a and b were recorded in CDCl$_3$, and spectrum c was recorded in deuterated DMSO.

The studies of EDA interaction provide valuable information on the interactions of polymer bounded fluorophores.[48−51] The formation of supramolecular structure based on EDA interaction between BDMA and pyrenyl groups on PPEGMA$_{13}$-*b*-PPyMA$_{24}$ was investigated in this research. The supramolecules were prepared by dissolving BDMA in THF solution of PPEGMA$_{13}$-*b*-PPyMA$_{24}$ and adding 6-fold of water into the polymer solution. After dialysis against water for 3 days the supramolecular structure in aqueous solution was obtained. BDMA is hydrophobic and sparingly soluble in water. However, the solubility of BDMA in water has increased significantly in the presence of PPEGMA$_{13}$-*b*-PPyMA$_{24}$, which indicates the formation of supramolecular structure in aqueous solution. There are two steps in the bimolecular electron transfer reaction: the first is the diffusion of the reactant to form the activated complex, and the second is the formation of products. ^{1}H nuclear magnetic resonance spectroscopy was employed in the study of the EDA interaction.[52] In ^{1}H NMR measurements the electron donor BDMA and electron acceptor PPEGMA$_{13}$-*b*-PPyMA$_{24}$ were

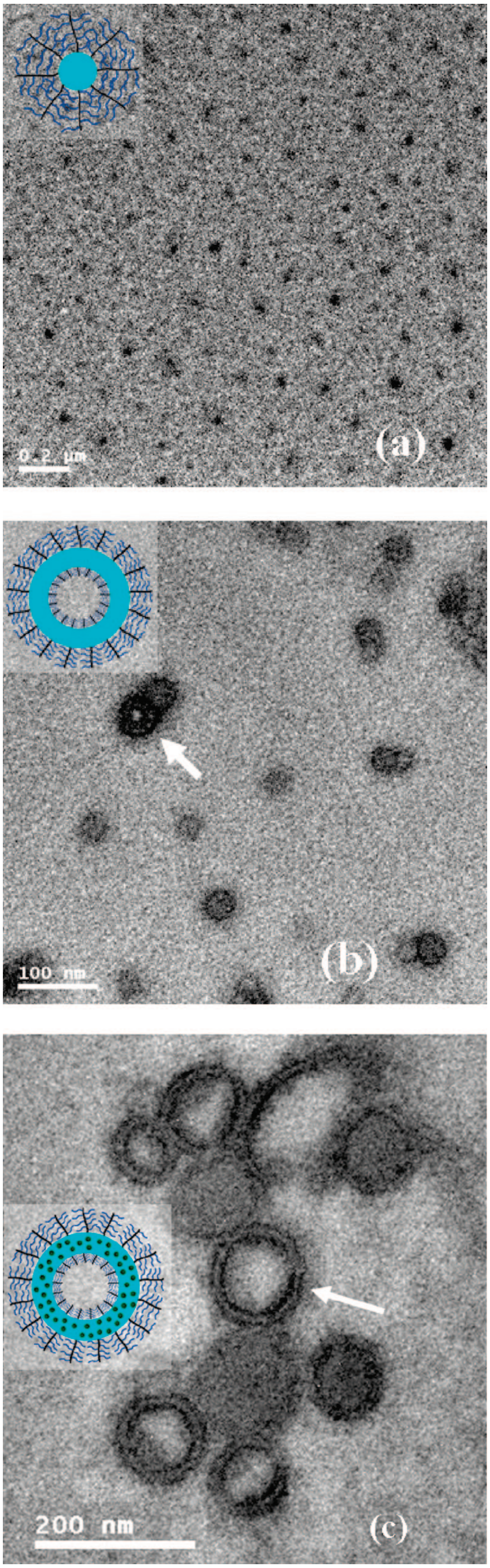


Figure 5. TEM images and schematic illustrations of self-assembly of comb block copolymers in aqueous solutions: (a) pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_6$ prepared by click reaction between pyrenyl azide (pyrenyl-N$_3$) and poly(poly(ethylene glycol) methacrylate)-*block*-poly(propargyl methacrylate) (PPEGMA$_{13}$-*b*-PPgMA$_6$) comb copolymer; (b) pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_{24}$; (c) supramolecular structure formed by PPEGMA$_{13}$-*b*-PPyMA$_{24}$ and 4-bromo-*N*,*N*′-dimethylaniline (BDMA). TEM specimens were prepared from their aqueous solutions and stained by RuO$_4$.

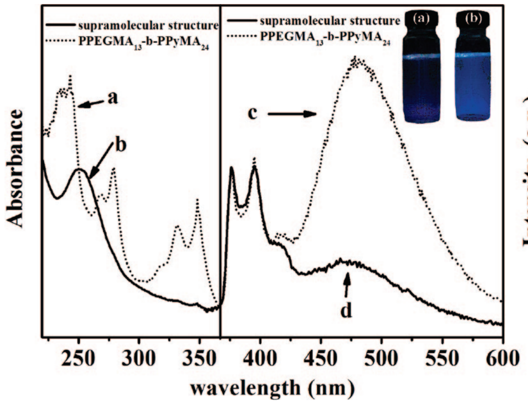


Figure 6. UV−vis spectra and fluorescence emission spectra (λ_{ex} = 315 nm) of pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_{24}$ (curves a, c) and supramolecules (curves b, d) in aqueous solutions. Emission spectra were normalized at 377 nm. The inset in the figure shows the images of supramolecules (vial a) and PPEGMA$_{13}$-*b*-PPyMA$_{24}$ (vial b) in aqueous solutions under UV light (λ = 365 nm). The concentrations of all the solutions were kept at 3.1 mg/mL.

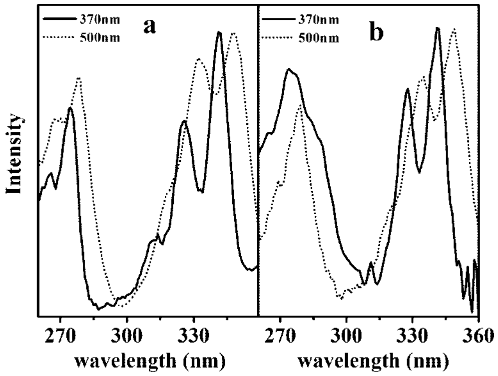
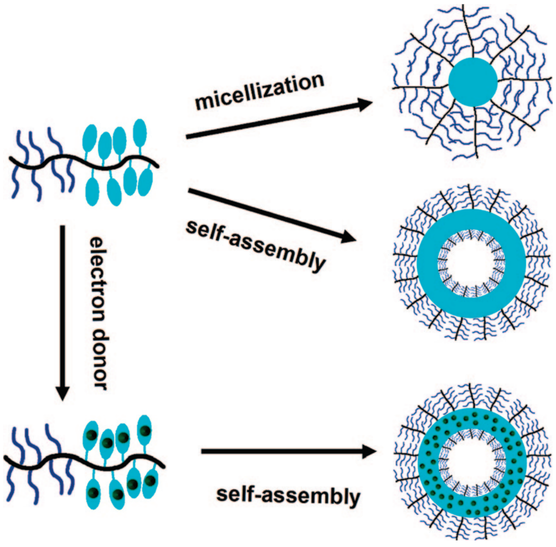


Figure 7. Fluorescence excitation spectra of (a) pyrene-bearing block copolymer PPEGMA$_{13}$-*b*-PPyMA$_{24}$ and (b) supramolecules in aqueous solutions (3.5 mg/mL) at 25 °C monitored at 370 nm (solid line) and at 500 nm (short dotted line).

Scheme 3. Schematic Representation for the Self-Assembly of the Comb Copolymers in Aqueous Solution



measured in CDCl$_3$. After water was removed by freeze-drying, the supramolecules formed by BDMA and PPEGMA$_{13}$-*b*-PPyMA$_{24}$ at solid state were prepared, and they cannot be dissolved in CDCl$_3$. However, they could be dissolved in deuterated DMSO, so supramolecules were measured in deuterated DMSO. In the ^{1}H NMR spectrum of BDMA there are three signals at 2.92, 6.59, and 7.31 ppm, which were attributed to the methyl protons on the tertiary amine groups ($-N(C\mathbf{H}_3)_2$) and protons at ortho and meta position of phenyl rings (Figure 4a). Spectrum c in Figure 4 is the ^{1}H NMR spectrum of supramolecular structure formed by BDMA and PPEGMA$_{13}$-*b*-PPyMA$_{24}$. After formation of the supramolecular structures, the signals of protons at ortho and meta positions of phenyl rings on BDMA were shifted to 6.73 and 7.34 ppm, and the signals of protons on pyrenyl groups showed a downfield shift of 0.10 ppm. The shifts of the signals were attributed to the EDA interaction between BDMA and pendant pyrenyl groups on PPEGMA$_{13}$-*b*-PPyMA$_{24}$. According to ^{1}H NMR results, the molar ratio of pyrenyl groups to BDMA was 2:1, so it was the EDA interaction that improved the solubility of BDMA in water. The equilibrium constant of the EDA interaction was determined based on Benesi−Hildebrand method.[53] The constant was calculated to be 96.1 L/mol (Supporting Information).

Figure 5 shows TEM images of the self-assembly aggregates of two comb copolymers and supramolecules formed by one comb copolymer and BDMA. The TEM specimens were prepared by depositing aqueous solutions on Foemvar grids; water was evaporated in air. The PPyMA blocks and BDMA were selectively stained by RuO$_4$. Figure 5a is a TEM image of PPEGMA$_{13}$-*b*-PPyMA$_6$ self-assembled in an aqueous solution. On the image spherical micelles with narrow size distribution were observed. The micelles are composed of hydrophobic PPyMA cores and hydrophilic PPEGMA coronae. The average diameter of the core is 10 nm, which corresponds to 2-fold of the extended molecular length of PPEGMA$_{13}$-*b*-PPyMA$_6$ (4.5 nm calculated by Chem. 3D), and an illustration for the micellar structure is shown in the inset of Figure 5a. Figure 5b is a TEM image of self-assembly of PPEGMA$_{13}$-*b*-PPyMA$_{24}$. The vesicular structure is evidenced from a higher transmission at the center of the aggregates than around their periphery.[54] A schematic representation for the vesicular structure in aqueous solution is shown in the inset of Figure 5b. In the vesicles, the hydrophobic PPyMA blocks constitute the vesicle wall, while the chains of soluble PPEGMA blocks extend from the inner and outer surfaces into water (inset in Figure 5b). These aggregates involve the looping of the hydrophobic blocks into the wall of the aggregates and the tailing of hydrophilic PPEGMA blocks to form the corona of the aggregates.[55] Moreover, from the TEM image displayed in Figure 5c, the supramolecular structure of PPEGMA$_{13}$-*b*-PPyMA$_{24}$ and BDMA is spherical and possesses morphology consistent with that of vesicles, which is in agreement with the morphological diagram reported previously.[56] We can examine closely on the contour curves and give an overall vesicle membrane thickness of 17 nm. The PPyMA block in PPEGMA$_{13}$-*b*-PPyMA$_{24}$ has an unperturbed end-to-end distance of 5.2 nm (calculated by Chem. 3D, Supporting Information), which indicates that the membrane is a bilayer structure with the PPyMA blocks extended to a certain extent. PPyMA blocks and BDMA were self-assembled into the walls of vesicles via the EDA interaction. The sizes of vesicle were polydispersed with the outside diameter ranging from 90 to 130 nm. However, the wall thickness of the vesicles was very uniform and independent of the overall sizes of the vesicles. It is worthy of note that the nanostructures were very stable; the size and the morphology were not changed after prolonged storage for up to several weeks.

The composition of the comb copolymer plays an important role in the self-assembly of PEGMA$_m$-*b*-PyMA$_n$ in aqueous solution. The comb copolymer chains with short hydrophobic blocks self-assemble into micellar structure, and the copolymer chains with long hydrophobic blocks self-assemble into vesicle structure. Bigger vesicles are formed when EDA interaction is involved in the system. The self-assembly of the comb copolymers in aqueous solution is illustrated in Scheme 3.

The UV−vis spectrum of PPEGMA$_{13}$-*b*-PPyMA$_{24}$ shows typical absorption bands of pyrene (curve a in Figure 6). The local microenvironment exerts influence on the spectral features of pyrenyl groups.[57] The absorption spectrum of the supramolecules showed a broad absorption peak with a maximum at 252 nm (curve b in Figure 6). The differences in absorption spectra indicate that the interaction between BDMA and pyrene is strong, and the new absorption band can be attributed to the occurrence of a ground-state charge-transfer (electron donor−acceptor) interaction.[58,59] The fluorescence emission spectrum of PPEGMA$_{13}$-*b*-PPyMA$_{24}$ excited at 315 nm exhibits “monomer” emissions at 376 nm due to isolated excited pyrenyl groups and a broad excimer emission centered at 480 nm (spectrum c in Figure 6).[60] The spectrum presents a relatively weak monomeric emission and a strong excimer band. The excimer emission is attributed to the intramolecular excimer formation.[32] Meanwhile the steady-state fluorescence spectrum of supramolecules shows quenched intensity (spectrum d in Figure 6). The inset of Figure 6 shows two images of aqueous solutions of supramolecules (vial a) and PPEGMA$_{13}$-*b*-PPyMA$_{24}$ (vial b) under UV light ($\lambda = 365$ nm). The images indicate that the solution in vial (b) shows very strong fluorescent properties, and the solution in vial (a) does not. The quenched emission spectrum of the supramolecules suggests the occurrence of EDA interaction between BDMA and pyrenyl groups and the close distance between BDMA and pyrenyl groups as a result of the encapsulation of BDMA by the hydrophobic PPyMA blocks in the wall of vesicles. The overall shape of the emission spectrum remains unchanged, and thus it rules out the possibility of any exciplex formation.[61−63] This result keeps consistent with a previous report that pyrene and BDMA are in general not considered as complex-forming components at the ground state.[64]

Excitation spectra in Figure 7 monitored at monomer emission (370 nm) and at excimer emission (500 nm) provide compelling evidence for ground-state interactions of pyrenes. The general features of the spectra of PPEGMA$_{13}$-*b*-PPyMA$_{24}$ and supramolecules in aqueous solutions are similar. However, comparing the spectra of PPEGMA$_{13}$-*b*-PPyMA$_{24}$ excited at 370 and 500 nm, 7 nm blue shift could be observed. For supramolecules a 8 nm blue shift was found (Figure 7). Compared to the spectrum monitored at the excimer emission, the blue shift of the spectrum monitored at the monomer emission means the excimer originates from aggregates of pyrenyl groups in the membrane of vesicles (PPEGMA$_{13}$-*b*-PPyMA$_{24}$ comb copolymer vesicles or supramolecular vesicles) prior to excitation.[65]

Conclusions

The combination of RAFT and click chemistry is a novel, effective, and promising strategy to design amphiphilic functional comb copolymers. The copolymers were able to form ordered aggregates in aqueous solutions. The comb copolymer with shorter PyMA hydrophobic block self-assembled into spherical micelles and the comb copolymer with longer hydrophobic block self-assembled into vesicles. TEM, ^{1}H NMR, UV−vis, and steady-state fluorescence results proved the presence of bimolecular EDA interaction between PEGMA$_{13}$-*b*-PyMA$_{24}$ and BDMA and formation of supramolecules in the membrane of vesicles. This work paves a way to the synthesis of a variety of novel comb-shaped copolymers with well-defined architectures and preparation of new supramolecular structure based on electron donor−acceptor interaction.

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Supporting Information Available: Supporting figures including experimental part, analysis of ^{1}H NMR results, and 3D model of CBC copolymer calculated by Chem. 3D. This material is available free of charge via the Internet at http://pubs.acs.org.

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