Synthesis of Conjugated−Ionic Block Copolymers by Controlled Radical Polymerization

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ABSTRACT: A novel series of well-defined amphiphilic block copolymers containing conjugated poly(fluorene) (PF) block and coillike poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) were successfully synthesized through atom transfer radical polymerization (ATRP) initialized by a 2-bromoisobutyrate end-capped PF macroinitiator using CuCl/HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine) as the catalyst. The first-order kinetics plot indicated a constant number of active species present in the polymerization. The molecular weight and molecular weight distribution were well controlled, implying well-defined block structure of the prepared block copolymers. The chemical structures of the copolymers were confirmed by ^{1}H NMR studies. The copolymers could be successfully quanternized, and the final conjugated−ionic block copolymers were found to form PF aggregates in water as confirmed by ^{1}H NMR, UV−vis, and photoluminescence (PL) spectra. PL spectra and quantum efficiency measurement also suggested the formation of excimers within the PF aggregates.

Introduction

Recently, novel film deposition techniques such as layer-by-layer self-assembly,[1] inkjet printing,[2] and screen printing[3] have been the subject of research as they find applications in fabrication of large-area electronic and photonic devices in a low-cost way. In these solvent-based approaches, the most attractive solvent is water. Therefore, the exploitation of novel optoelectronic polymeric materials with water processability is of considerable interest from both theoretical and practical points of view. One approach is to employ ionic conjugated polymers which are water-soluble due to the charged functionalities attached. For example, water-soluble poly(phenylenevinylene) (PPV),[4] polyphenylene (PP),[5] poly(phenyleneethynylene) (PPE),[6] and polythiophene (PT)[7] have been obtained recently with either cationic or anionic subsititution. Alternatively, a miniemulsion approach was suggested for those nonionic conjugated polymers in the construction of multilayer assemblies through aqueous medium.[8] Polymeric nanoparticles with a dimension of tens to hundreds of nanometers could thus be produced with the aid of surfactants.

Amphiphilic conjugated block copolymers composed of mutually repulsive and chemically connected conjugated-coil segments with different hydrophilicities may self-assembly into highly ordered periodical geometries in selective solvents.[9] Because the self-assembly process gives rise to the formation of various nanostructures with semiconducting characteristics, amphiphilic conjugated block copolymers may be promising to serve as unique optoelectronic materials. For example, Wang et al. studied amphiphilic rod−coil block copolymers containing oligo-PPV (OPV) rod and poly(ethylene glycol) (PEG) coil which were found to form cylindrical micelles in THF and THF/water mixture.[10] Jenekhe et al. observed honeycomb morphologies upon casting CS_2 solution of poly(phenylquinoline)-*b*-poly(styrene) (PPQ−PS) copolymers.[11] The same materials were also found to self-assembly into micelles with different shapes by controlling the solvent mixture and drying rate.[12] While self-assembly of amphiphilic conjugated polymers has been performed from organic solvents or solvent/water mixtures, the formation of ordered objects in water using these materials is still a major concern which necessitates the synthesis of novel amphiphilic systems with improved water processability.

Poly(fluorene) (PF) is known as a high-performance blue-light-emitting polymer with excellent chemical and thermal stability.[13] Unfortunately, most PF derivatives are only soluble in organic solvents which limits the application of PF in water-based events. Although a few ionic PF[14] and PF aqueous dispersions[8] have been obtained, the preparation of PF-based amphiphilic block copolymers is still a challenge. To date, such rod−coil type polymeric systems mainly employed either a condensation of two or three prefabricated blocks or a macroinitiator to carry out further chain propagation of other blocks. In the latter approach, controlled polymerization techniques including nitroxide-mediated radical polymerization (NMRP)[15] and atom transfer radical polymerization (ATRP)[16] are often utilized due to the advantages of wide selection of monomers and tolerable reaction conditions. Here we report our successful application of ATRP to obtain well-defined amphiphilic conjugated block copolymers with poly(fluorene) (PF) as the conjugated rod and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) as the telechelic coils, as shown in Scheme 1. PDMAEMA has been extensively used as a hydrophilic block in many amphiphilic systems.[17,18] The resulting copolymers could

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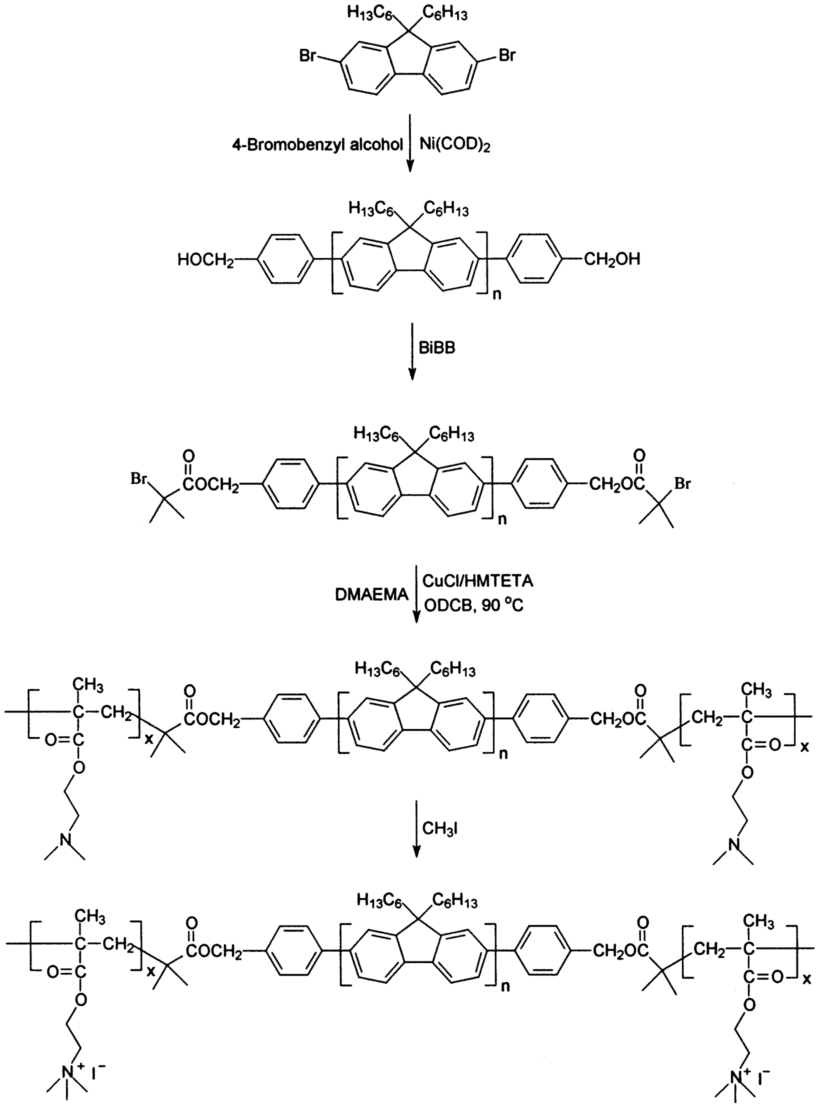
Scheme 1. Synthetic Route for the Conjugated−Ionic Triblock Copolymers



be facilely quaternized to produce conjugated−ionic block copolymers which strongly enhanced their hydrophilicity.[18] The self-assembly behavior of such conjugated−ionic systems is also discussed.

Experimental Section

Materials. 2,7-Dibromofluorene (97%), 1-bromohexane (98%), 4-bromobenzyl alcohol (99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%), 2-bromoisobutyryl bromide (BiBB) (98%), CuCl (99.995+%), 1,5-cycooctadiene (COD) (99%+), and bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$) were purchased from Aldrich Chemical Co. and were used as received. *N*,*N*-Dimethylformamide (DMF, 99.9%, TEDIA), dichloromethane (99.9%, TEDIA), and *o*-dichlorobenzene (ODCB) (99%, Merck) were distilled from calcium hydride (CaH$_2$) and stored under argon. Tetrahydrofuran (99.8%, TEDIA) and toluene (99.5%, Merck) were distilled from sodium/benzophenone. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (98%, Aldrich) was passed through a column of alumina to remove inhibitor and dried over CaH$_2$. It was then distilled at reduced pressure and stored under argon. The monomer 2,7-dibromo-9,9-di-*n*-hexylfluorene was prepared according to a literature procedure.[19]

Measurements. NMR spectra were collected on a Bruker Avance 400 spectrometer with tetramethylsilane as the internal standard. FTIR spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr disks. Elemental microanalyses were carried out by the Microanalysis Lab of the National University of Singapore. UV−vis spectra were recorded on a Shimadzu 3101 spectrophotometer. The concentrations of the copolymer solutions were adjusted to about 0.01 mg/mL or less. Size exclusive chromatography analysis was conducted with a Waters 2690 separation module equipped with a Waters 2410 differential refractometer HPLC system and three 5 μm Waters Styragel columns (pore size: 10^3, 10^4, and 10^5 Å) in series, using polystyrene as the standard and THF as the eluant at a flow rate of 1.0 mL/min and 35 °C.

Fluorescence measurement was carried out on a Perkin-Elmer LS 50B luminescence spectrometer with a xenon lamp as a light source. The fluorescence quantum yields (Φ_f) of the polymers in solutions were recorded by using the diluted quinoline solution in 0.1 N H_2SO_4 as the standard, assuming that the fluorescence quantum yield was 0.546 with the excitation wavelength of 365 nm. Φ_f was calculated according to the following equation:

$$\Phi_S = \Phi_R\left(\frac{A_R}{A_S}\right)\left(\frac{I_S}{I_R}\right)\left(\frac{{n_S}^2}{{n_R}^2}\right)$$

where Φ_R and Φ_S are the fluorescence quantum yields of quinoline and the polymers, respectively, A_R and A_S are the absorbances of quinoline and the polymers at the excitation wavelength, respectively, I_R and I_S are the integrated emission intensities of quinoline and the polymers, respectively, and n_R and n_S are refractive indices of the corresponding solvents of the solutions, respectively (pure solvents were assumed).

Synthesis of Hydroxy-Functionalized PF (PFOH).[19,20] In a 250 mL flask, $\mathrm{Ni(COD)_2}$ (3.90 g, 14.2 mmol), COD (1.75 mL, 14.2 mmol), and bipyridine (2.22 g, 14.2 mmol) were mixed in 10 mL of anhydrous DMF under argon. The dark blue solution was stirred at 70 °C for half an hour, and then 2,7-dibromo-9,9-di-*n*-hexylfluorene (3.20 g, 6.50 mmol) and 4-bromobenzyl alcohol (0.608 g, 3.25 mmol) in 60 mL of anhydrous toluene were added. The reaction was heated at 85 °C in dark for 2 days. After cooling, the mixture was diluted with 100 mL of THF, and aqueous hydrazine solution was introduced. The resulting mixture was stirred overnight, and the aqueous layer was separated and extracted with THF. The combined organic layers was filtered, concentrated, and poured into 400 mL of methanol. The solid was collected, purified by Soxhlet extraction with methanol, and reprecipitated into methanol to give final product as yellow powder (1.60 g, 64% yield) with M_n of 2900 (SEC) and 2900 (^{1}H NMR) and M_w/M_n of 1.6. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 7.65−7.9 (br, fluorene aromatic protons), 7.61, 7.52 (2 d, phenyl end groups), 4.81 (s, $\mathrm{PhC}H_2\mathrm{O}-$), 2.13 (br, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$), 1.3−0.7 (m, $-\mathrm{CH_2C_5}H_{11}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 151.8 (fluorene q-C), 141.3 (w), 140.6 (fluorene q-C), 140.2 (w), 140.0 (fluorene q-C), 139.8 (w), 139.7 (w), 127.5 (phenylene H−C), 127.4 (phenylene H−C), 126.2 (fluorene H−C), 121.5 (fluorene H−C), 119.9 (fluorene H−C), 65.2 (C−OH), 55.3 (Ph−C−Ph), 40.4 ($\mathrm{CH_2}$), 31.5 ($\mathrm{CH_2}$), 29.7 ($\mathrm{CH_2}$), 23.9 ($\mathrm{CH_2}$), 22.5 ($\mathrm{CH_2}$), 14.0 ($\mathrm{CH_3}$). FT-IR (KBr, $\mathrm{cm^{-1}}$): 3060, 3025 ($\upsilon_{\mathbf{=C-H}}$); 2960, 2927, 2854 ($\upsilon_{\mathbf{-C-H}}$); 1610 ($\upsilon_{\mathbf{C=C}}$); 1459 ($\delta_{\mathbf{-C-H}}$); 1189 ($\upsilon_{\mathbf{-C-O}}$); 813 ($\delta_{\mathbf{=C-H}}$). Elem. Anal. Calcd (assuming 8 repeating units according to ^{1}H NMR end-group analysis): C, 89.46; H, 9.42. Found: C, 89.37; H, 9.57.

Synthesis of PF Macroinitiators. PFOH (1.63 g, 0.54 mmol), triethylamine (4.4 mL, 31 mmol), and dry $\mathrm{CH_2Cl_2}$ (40 mL) were placed in a 150 mL round-bottomed flask. After cooling to 0 °C, 2-bromoisobutyryl bromide (3.6 mL, 26 mmol) was added dropwise with vigorous stirring under an argon atmosphere. The temperature was allowed to rise to 20 °C, and the reaction mixture was stirred overnight. The solution was extracted with water to remove the salt and the excess of bromoisobutyryl bromide. After being dried over anhydrous sodium sulfate, the clear solution was concentrated, and bromo-ended PF macroinitiator was precipitated in methanol. After filtration, the solid was rinsed with methanol sufficiently and passed through a short column using toluene as the eluent. After it was dried under vacuum at 40 °C, 1.6 g of faint yellow product was obtained (85% in yield) with M_n of 3100 (SEC) and 3000 (^{1}H NMR) and M_w/M_n of 1.5. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 7.65−7.9 (br, ring aromatic protons), 7.63, 7.53 (2 d, phenyl end groups), 5.31 (s, $\mathrm{Ph-C}H_2\mathrm{O}-$), 2.1 (br, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$), 2.0 (s, $-\mathrm{C(C}H_3\mathrm{)_2Br}$), 1.3−0.7 (m, $-\mathrm{CH_2C_5}H_{11}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 171.6 (C═O), 151.8 (fluorene q-C), 141.8 (w), 140.5 (fluorene q-C), 140.0 (fluorene q-C), 139.4 (w), 134.2 (w, phenylene q-C), 128.4 (phenylene H−C), 127.3 (phenylene H−C), 126.1 (fluorene H−C), 121.5 (fluorene H−C), 119.9 (fluorene q-C), 67.4 (Ph−C−O), 55.3 (Ph−C−Ph), 40.3 ($\mathrm{CH_2}$), 31.4 ($\mathrm{CH_2}$), 30.8 ($\mathrm{CH_3}$), 29.6 ($\mathrm{CH_2}$), 23.8 ($\mathrm{CH_2}$), 22.5 ($\mathrm{CH_2}$), 14.0 ($\mathrm{CH_3}$). FT-IR (KBr, $\mathrm{cm^{-1}}$): 3059, 3026 ($\upsilon_{\mathbf{=C-H}}$); 2960, 2926, 2854 ($\upsilon_{\mathbf{-C-H}}$); 1737 ($\upsilon_{\mathbf{C=C}}$), 1458 ($\delta_{\mathbf{-C-H}}$); 1156, 1105 ($\upsilon_{\mathbf{-C-O-C}}$); 813 ($\delta_{\mathbf{=C-H}}$). Elem. Anal. Calcd (assuming 7 repeating units according to ^{1}H NMR end-group analysis): C, 83.32; H, 8.80. Found: C, 83.96; H, 8.73.[21]

Synthesis of PDMAEMA−PF−PDMAEMA Triblock Copolymers by ATRP. PDMAEMA-*b*-PF-*b*-PDMAEMA triblock copolymers were synthesized by solution polymerization in *o*-dichlorobenzene. In a typical run, a glass tube was charged with 0.05 g (0.018 mmol) of PF macroinitiator and 3.6 mg (0.036 mmol) of CuCl before it was sealed with a rubber septum. The tube was degassed with three vacuum−argon cycles to remove air and moisture, and then *o*-dichlorobenzene (0.80 mL) and HMTETA (9.8 μL, 0.036 mmol) were added with syringes. The glass reactor was immersed in an oil bath at 90 °C, and a clear solution with light green color formed within a few seconds. Upon dissolution, 0.80 mL (4.8 mmol) of DMAEMA was quickly injected into the tube to carry out the polymerization. Samples for ^{1}H NMR and SEC characterization were taken out from the reaction mixture at time intervals. The conversion was determined by comparing the relative integrations of the peaks at 4.09 and 4.28 ppm in ^{1}H NMR, which were attributed to $-\mathrm{OC}\boldsymbol{H}_2\mathrm{CH_2}-$ for polymer and monomer, respectively. The samples were passed through a column of neutral alumina to remove the catalysts. The polymers were precipitated into excess of hexane and dried in a vacuum at 40 °C. Light yellow powdery to glassy samples were obtained.

Table 1. ATRP Results of DMAEMA Initiated by PF Macroinitiator[a]

sample	[M]/[I][b]	time (min)	conv (%)	$M_{n,\mathrm{theo}}$	$M_{n,\mathrm{NMR}}$	$M_{n,\mathrm{SEC}}$	M_w/M_n
P1	66	60	90	12 300	15 600	16 800	1.23
P2	107	60	89	17 980	20 300	18 500	1.22
P3	178	105	80	25 900	31 600	26 100	1.21
P4	265	50	63	29 100	21 300	20 900	1.26
P5	265	58	67	30 810	35 100	29 700	1.26
P6	265	90	76	34 600	35 800	30 200	1.33
P7	265	108	84	36 900	38 700	34 700	1.23

[a] [HMTETA]:[CuCl]:[I] = 2:2:1; ratio of monomer (DMAEMA) vs solvent (*o*-dichlorobenzene) in volume was 1:1. All the reactions were conducted at 90 °C. [b] [I] is defined as the molar concentration of PF macroinitiator containing 7 fluorene units and two benzene rings with initiating groups (DMAEMA = 2-(dimethylamino)ethyl methacrylate; PF = poly(fluorene); HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine.)

Quaternization of PDMAEMA−PF−PDMAEMA Triblock Copolymers.[18] Typically, 0.19 g of PDMAEMA−PF−PDMAEMA triblock copolymer P3 (Table 1) was dissolved in 50 mL of dry THF, and methyl iodide was added to the above solution at room temperature. The molar ratio of the methyl iodide/DMAEMA units was adjusted to about 2. The mixture was stirred overnight, and acetone was added. The light yellow precipitate was collected and washed with acetone for several times to remove the excess of methyl iodide. The samples were then dried at 40 °C in a vacuum, and light yellow powders were obtained (yield >90%). ^{1}H NMR (DMSO, ppm): δ 8.1−7.8 (br, fluorene aromatic protons), 7.7, 7.5 (br, phenyl end groups), 4.4 (s, $\mathrm{O-C}H_2-$), 3.9 (s, $\mathrm{N-C}H_2-$), 3.33 (s, $\mathrm{N-(C}H_3\mathrm{)_4}$), 1.7−2.3 (br, $-\mathrm{C}H_2\mathrm{C_5H_{11}}$ and $-\mathrm{C}H_2\mathrm{-C(CH_3)}$), 1.1 and 0.7 (br, $-\mathrm{CH_2C_5}H_{11}$), 0.9 (br, $-\mathrm{CH_2C(C}H_3\mathrm{)}$).

Results and Discussion

Poly(fluorene)-based triblock copolymers have been synthesized previously through a one-pot reaction.[22] However, such an approach may encounter the problem that those triblock molecules containing relatively short rigid segments within the products cannot be removed easily. A more reasonable way is to prepare the PF macroinitiator with suitable initiating functionalities for ATRP, and molecular impurities can be removed at this stage. For this purpose, a PF polymer end-capped with hydroxy groups was prepared by using a Ni(0) catalyst through an intermolecular Yamamoto-type condensation. 4-Bromobenzyl alcohol as the end-capper not only serves to functionalize the ends of the PF chain but also plays a role in controlling the polymerization degree (PD) in a statistical fashion. As a result, the M_n of the PF could be limited to around 3000. Such a molecular weight is reasonable as it offers enough solubility for PF in the reaction mixture at enhanced temperature, which is critical to initiate further ATRP. Esterification of the above polymer with 2-bromoisobutyryl bromide afforded our final macroinitiator. 2-Bromoisobutyrate derivatives have proven versatile for ATRP of many vinyl monomers.[16] The structures of both PFOH and the PF macroinitiator were confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopy. Figure 1 shows the ^{1}H NMR spectra of PFOH and the PF macroinitiator. The distinct peaks exhibited in both spectra between 7.50

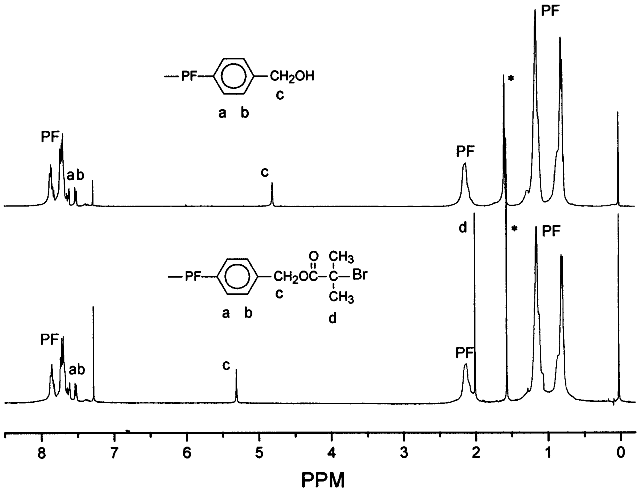


Figure 1. ^{1}H NMR spectra of hydroxy-functionalized poly(fluorene) and poly(fluorene) macroinitiator (* H_2O).

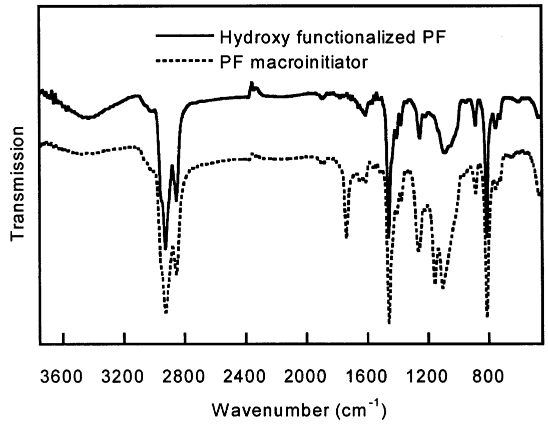


Figure 2. FTIR spectra of hydroxy-functionalized poly(fluorene) and poly(fluorene) macroinitiator.

and 7.65 ppm clearly show the successful incorporation of the end-capping phenylene groups. In addition, compared with Figure 1a, Figure 1b shows thorough suppression of the resonance for Ph−C$\boldsymbol{H}_2$−OH at 4.81 ppm and appearance of a single resonance for Ph−C$\boldsymbol{H}_2$−OC=O at 5.31 ppm, indicating a complete transformation of the hydroxy into bromoisobutyrate functionality in the macroinitiator. The FTIR spectrum of the PF macroinitiator is compared with that of PFOH in Figure 2. The appearance of the peak at 1737 cm^{-1} for the PF macroinitiator also proves the successful functionalization with 2-bromoisobutyrate in the end of the macroinitiator chain. The PD of the PF macroinitiator was estimated through comparing the relative integrations of total aromatic protons and the methylene protons (Ph−C$\boldsymbol{H}_2$−OC=O). Thus, the number-average PD of the PF macroinitiator was calculated to be about 7, which is close to the result from SEC measurement.[20]

ATRP of DMAEMA was conducted at 90 °C in *o*-dichlorobenzene solution with CuCl/HMTETA as the catalytic system.[23] A linear relationship was observed in the first-order kinetic plot (Figure 3), indicating the presence of a constant number of the growing species during the polymerization. It is proposed that halogen exchange would occur between chlorine and terminal bromine when CuCl is used as catalyst in a bromine-ended initiation system, which results in the formation of chlorine-ended polymer chains as the reaction proceeds.[23] Such a halogen exchange would make initiation faster than propagation and be beneficial to ATRP. The linear increase of the molecular weight and narrow molecular weight distribution (MWD) of the resulting copolymers supports the controlled fashion of the ATRP of DMAEMA, as showed in Figure 4. Because the macroinitiator was obtained through a step-growth polymerization approach where the molecular weight is controlled by the ratio of the end-capper instead of the polymerization mechanism, the PF macroinitiator presented a poorly controlled MWD (M_w/M_n was as high as 1.5). However, all of the copolymers obtained by ATRP showed relatively narrow MWD (Table 1). The considerable decrease of MWD values of the block copolymers compared with that of the macroinitiator should be attributed to the well-defined PDMAEMA chains existing in the copolymers. Table 1 summarizes the ATRP results of the copolymers.

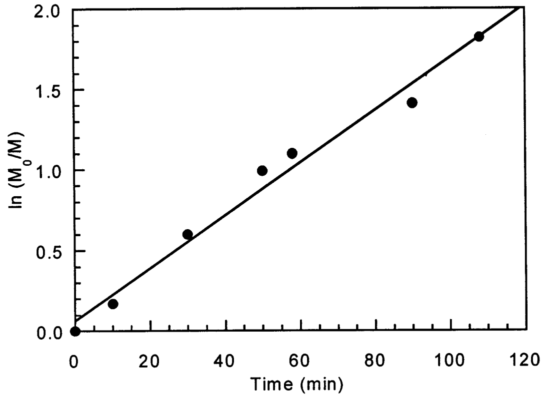


Figure 3. ln([M]$_0$/[M]$_t$) vs polymerization time for ATRP of DMAEMA with [poly(fluorene)]:[CuCl]:[HMTETA]:[DMAEMA]$_0$ = 1:2:2:265, 50 vol % in *o*-dichlorobenzene, 90 °C (DMAEMA = 2-(dimethylamino)ethyl methacrylate; HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine).

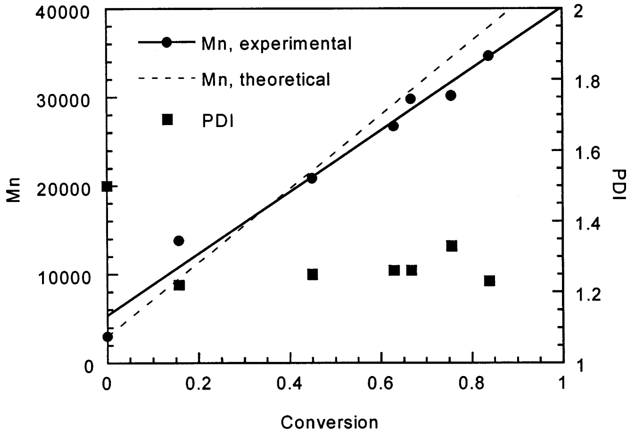


Figure 4. Dependence of molecular weight (SEC) and molecular weight distribution (PDI) on monomer conversion for ATRP of DMAEMA with [poly(fluorene)]:[CuCl]:[HMTETA]:[DMAEMA]$_0$ = 1:2:2:265, 50 vol % in *o*-dichlorobenzene, 90 °C (DMAEMA = 2-(dimethylamino)ethyl methacrylate; HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine; PDI = polydispersity index).

The formation of block structures can be evidenced by SEC measurement. Figure 5 shows the SEC profiles of the PF macroinitiator and four copolymer samples prepared using CuCl/HMTETA as the catalyst. The SEC curves corresponding to the respective block copolymers shifted to high molecular weights with the increase of monomer conversion, implying a well-controlled polymerization. All of the SEC traces gave symmetrical shapes

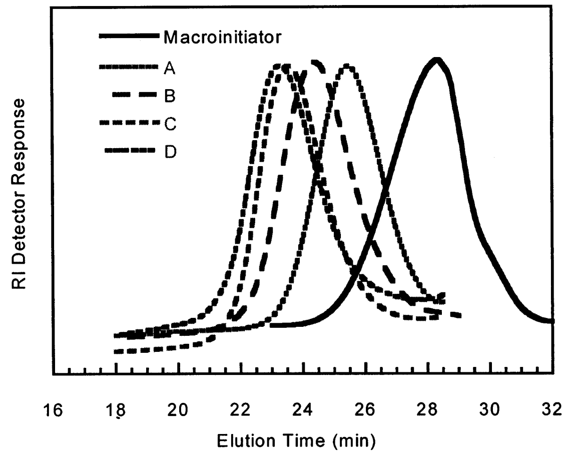


Figure 5. SEC traces of poly(fluorene) macroinitiator and triblock copolymers: (A) conversion = 16%, M_n (SEC) = 13 800, M_w/M_n = 1.22; (B) conversion = 45%, M_n (SEC) = 20 900, M_w/M_n = 1.25; (C) conversion = 67%, M_n (SEC) = 29 700, M_w/M_n = 1.26; (D) conversion = 84%, M_n (SEC) = 34 700, M_w/M_n = 1.23. Reaction conditions: [poly(fluorene)]:[CuCl]:[HMTETA]:[DMAEMA]$_0$ = 1:2:2:265, 50 vol % in *o*-dichlorobenzene, 90 °C (DMAEMA = 2-(dimethylamino)ethyl methacrylate; HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine).

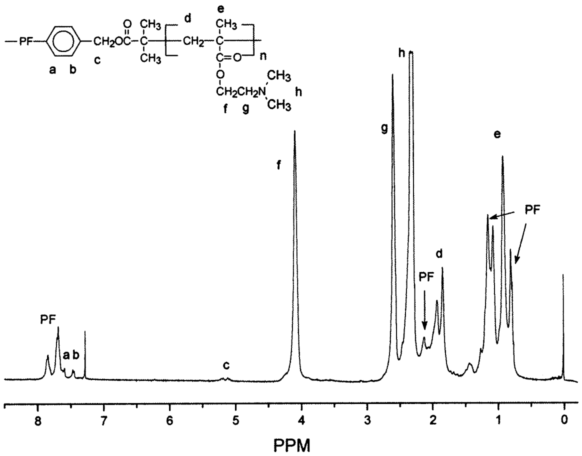


Figure 6. ^{1}H NMR spectrum of PDMAEMA−PF−PDMAEMA triblock copolymer in $CDCl_3$ (PDMAEMA = poly(2-(dimethylamino)ethyl methacrylate); PF = poly(fluorene)).

without shoulder, indicating the efficient initiation of DMAEMA by the PF macroinitiator from both ends. Hence, monoinitiation, which may result in bimodal molecular weight distribution, can be negligible. Moreover, in all SEC profiles of the block copolymers, no peak at the retention time for the macroinitiator was observed, indicating that well-functionalized macroinitiator was prepared at the first stage and relatively complete incorporation of the macroinitiator into the final copolymers has been achieved. These results clearly prove the successful preparation of the triblock copolymers.

The structures of the block copolymers were confirmed by ^{1}H NMR (Figure 6). The signals from the aromatic protons of the block copolymers are almost identical to those of the PF macroinitiator except for the slightly different chemical shifts of the end phenyl protons due to the change in the neighboring chemical environment after polymerization. In Figure 7, the proton absorption for Ph−C$\boldsymbol{H}_2$−OC=O at 5.31 ppm arising from the PF macroinitiator thoroughly disappeared, and two new split peaks could be observed at 5.1−5.3 ppm, which gave almost the same integration value as that for the peaks at 7.44−7.47 ppm ascribed to the end phenyl protons. These results strongly suggest the formation of well-defined block copolymers through ATRP with efficient initiation of DMAEMA and perfect intactness of PF backbone. The resulting copolymers were readily soluble in many common solvents including $CHCl_3$ and THF; however, they could not be dissolved in water directly.

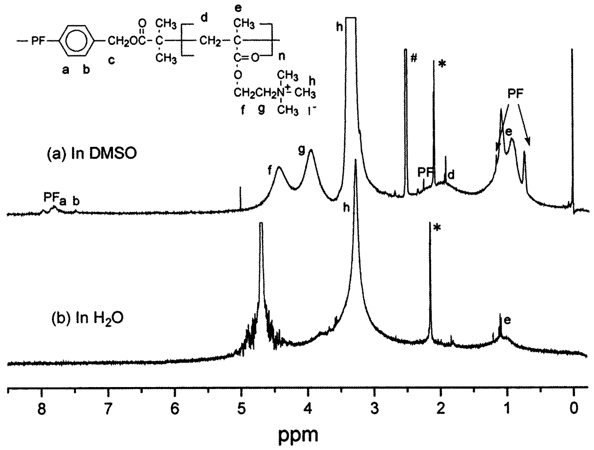


Figure 7. ^{1}H NMR spectra of quaternized PDMAEMA−PF−PDMAEMA triblock copolymer in (a) DMSO-d_6 and (b) D_2O (* CH_3COCH_3; # DMSO) (PDMAEMA = poly(2-(dimethylamino)ethyl methacrylate); PF = poly(fluorene)).

To improve the hydrophilicity, the copolymers were quaternized with methyl iodide. The reaction was very fast with white precipitation forming within 1 h at room temperature. Figure 7a shows the ^{1}H NMR spectra of the quaternized triblock copolymer (PFDMA-Q). It can be seen that a new peak is exhibited at 3.35 ppm due to the successful quaternization of the amine residues in the PDMAEMA blocks. PFDMA-Q showed good solubility in polar solvents such as DMSO. In water, PFDMA-Q also formed clear solutions. However, with the increase of the concentration of PFDMA-Q, the mixture tended to show an increased viscosity. For example, QP3 (quaternized P3) formed a very viscous solution at a weight concentration of 2%. The length of the hydrophilic segments was also found to affect the dissolution behavior of the copolymers. Copolymers with long hydrophilic segments such as QP3 could be dissolved in water more rapidly (1 day) than those with short hydrophilic segments such as QP1 (quaternized P1, 1 week). These observations suggest that the polymers could self-assemble in aqueous solution.[24] Because of the dramatically different solubility of PF and quaternized PDMAEMA chains, the rigid PF blocks would aggregate to form insoluble domains in water. Such an assumption was substantiated by ^{1}H NMR measurement. It is well established that NMR is an important tool for detecting the formation and structures of micelles in the solution of block copolymers. Figure 7b shows the ^{1}H NMR spectrum of PFDMA-Q in water. It can be seen that all of the peaks which are attributed to PF block disappear completely, indicating that PF blocks cannot be dissolved in water on a molecular level. We suggest that in water these conjugated−ionic block copolymers form PF aggregates which may be stabilized by the surrounding quaternized PDMAEMA blocks to minimize the contact surface of the hydrophobic domains with water. Such aggregates may also act as "physics links" in the solution of the

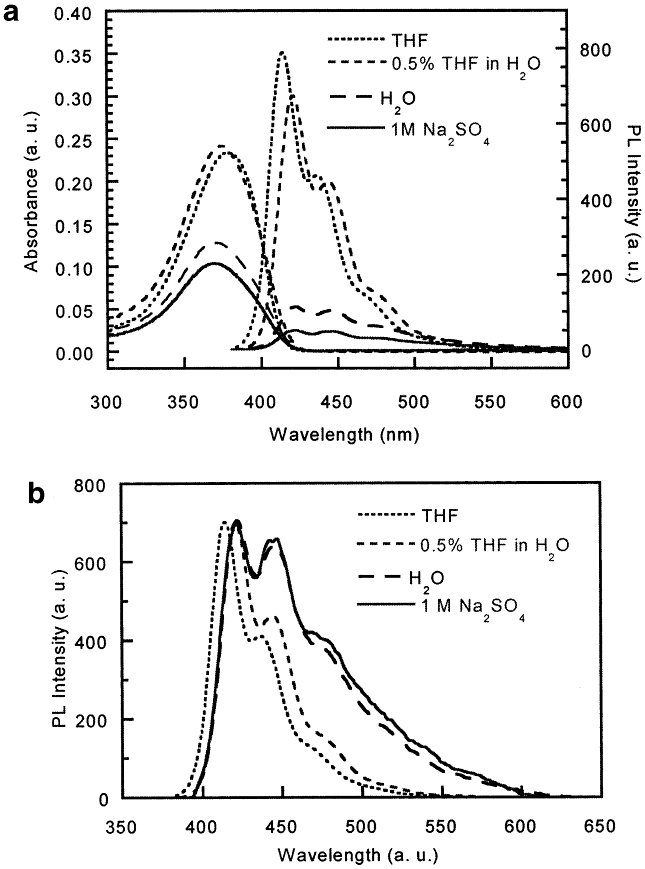


Figure 8. (a) UV−vis absorption and photoluminescence spectra of P1 in THF, water contain 0.5% THF and QP1 in water and 1 M Na_2SO_4 solution. (b) Normalized PL spectra.

copolymers, resulting in a remarkably enhanced viscosity.

Figure 8 shows the absorption and emission spectra of the neutral triblock copolymers (P1) in different solvents and solvent mixtures. In absorption spectra, the neutral sample in water/THF (water containing 0.5% THF) presents a blue-shifted peak at 374 nm compared with that in THF (379 nm). In addition, while the emission spectra in THF and in water/THF are similar in shape, the band is slightly broadened in the latter case with a prominent red shift from 414 to 422 nm. Besides, the copolymer in THF/water exhibited lower quantum efficiency (49%) than that in THF (83%). The red-shifted emission band and decreased quantum efficiency in water are in agreement with the existence of interchain interactions for PF blocks.

The photoproperty QP1 is also shown in Figure 8. It can be seen that QP1 exhibits a more blue-shifted absorption maximum in water (369 nm) than that of P1 in water/THF. Such a blue shift in the absorption spectra which was observed for both P1 and QP1 may imply comformation bending on the PF backbone in the poor solvent such as water, resulting in a decreased effective conjugation length. Although PF was found to present a more extended conformation under some conditions which gave rise to an additional sharp absorption at long wavelength (437 nm),[25] the conformation folding in poor solvent has recently been suggested for another conjugated polymer MEH−PPV based on the observation of blue-shifted absorption.[26] As a matter of fact, such a conformation variation is adopted by some flexible ABA triblock copolymers to form collapsed core in selective solvents.[27] More prominent spectral modification was observed when emission properties of QP1 was investigated. While QP1 presented similar emission maximum occurring at 422 nm to that of P1 in water/THF, an additional featureless emission band appeared at longer wavelength (500−600 nm), which is ascribed to excimer formation as there was no noticeable difference between the excitation spectrum of long wavelengh band (525 nm) and that for the excitonic band (422 nm). Although the appearance of such excimer emission is very common for PF polymers upon heating,[19,28,29] our findings suggest that the formation of excimers may be facilitated in PF aggregates in which tight intermolecular packing would occur due to the strong hydrophobic interactions. The formation of excimers in turn resulted in dramatically decreased quantum efficiency (0.26) for QP1 in water. In addition, the relative intensity of the first (422 nm) and the second (446 nm) vibrational band in the emission spectrum was reduced as compared with that of P1. These results are due to the excimer formation which offer additional channel of nonradiative decay and the energy migration from the higher energy level to the trapping sites (excimers).[30] It was also found that improvement of ionic strength of the solution lead to further decrease in the quantum efficiency. For example, in 1 M Na_2SO_4 solution, QP1 exhibited a slightly increased long wavelength emission and in turn a decreased quantum efficiency of 0.16 (Figure 8), indicating enhanced interchain interactions under these conditions. At present, however, the detailed excimer formation mechanism related to the aggregation growth remains our major concern which requires further information on size and geometries of the aggregates, local chromophore alignments, and molecular motions.

Conclusion

In summary, amphiphilic PDMAEMA−PF−PDMAEMA triblock copolymers have been successfully prepared by atom transfer radical polymerization through a macroinitiator approach. The PF macroinitiator was prepared and characterized by ^{1}H NMR, ^{13}C NMR FTIR, and elemental analysis and proved efficient for the ATRP of DMAEMA. The first-order kinetics plot was linear, and the molecular weights and their distributions were relatively controlled, indicating the “living” nature of the polymerization. The copolymer could be successfully quaternized, and the resulting rod−ionic triblock copolymer formed PF aggregates in water as confirmed by ^{1}H NMR, UV−vis, and photoluminescence spectra. Excimers were found to exist in the PF aggregates as was evidenced by the appearance of an additional long wavelength emission band and the decreased quantum efficiency. Such a supramolecular system containing conjugated polymers may offer an opportunity for developing new optoelectronic devices and nanocomposites.

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