Synthesis and Self-Assembly of Polyhydroxylated and Electropolymerizable Block Copolymers

Satyananda Barik, Suresh Valiyaveettil

Department of Chemistry, 3 Science Drive 3, National University of Singapore, 10 Kent Ridge Crescent, Singapore 117543
Correspondence to: Dr. S. Valiyaveettil (E-mail: chmsv@nus.edu.sg)

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ABSTRACT: A facile synthetic strategy for preparing hydroxylated polymethacrylate amphiphilic block copolymers (PCzMMA-*b*-PBMMA, PFlMMA-*b*-PBMMA) incorporated with primary and secondary hydroxyl groups and electroactive moieties along the polymer backbone is reported. Full characterization, structure-property relationship and self-assembly of these polymers are discussed. Due to interplay of hydrophobic/hydrophilic interactions, PCzMMA-*b*-PBMMA formed a layered lattice and PFlMMA-*b*-PBMMA showed a vesicular morphology. Electropolymerization of the electroactive units led to the formation of cross-conjugated polymer network in solution and in thin films. The network structure was characterized with a range of spectroscopic techniques. Such highly processable polymers may be of interest to applications in which a conducting amphiphilic films with strong adhesion to various substrates are required. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2217–2227

KEYWORDS: amphiphilic block copolymers; atom transferôradical polymerization (ATRP); electropolymerization; polyhydroxylated polymers; self-assembly

INTRODUCTION The self-assembly of block copolymers has gained much attention owing to the presence of long range ordering in the polymer lattice to form highly ordered micelles,[1] cylindrical rods,[2] long fibers, tubes or vesicles.[1–6] Multiple factors such as hydrophilic or hydrophobic nature, block lengths, and interaction of various functional groups leading to miscibility or phase separation inside the polymer lattice are responsible for the formation of interesting morphologies.[7–10] Hydrophilic polymers based on telechelic polyethylene glycol, 2-ethyl-(2-pyrrolidine)methacrylate, poly(2-hydroxyethyl methacrylate), and other polymers bearing primary hydroxyl groups on the side chain have been reported.[4] Poly(vinyl alcohol) and its copolymers have been extensively used for preparing stable hydrogels and interpenetrating networks.[11]

Amphiphilic block copolymers are interesting owing to their applications in drug encapsulation,[12] adhesives,[13] coatings,[14] and stable gels.[15,16] Block copolymers have been extensively studied due to their unusual morphologies in solution and in solid state.[17–22] Solketal-based monomers offer a facile route for obtaining multihydroxylated hydrophilic polymers[21] and incorporation of electroactive groups helps to prepare conjugated polymer network (CPN) for enhancing the conductivity of the polymer lattice through electropolymerizaton.[22,23]

Here, we report synthesis, characterization of polyhydroxylated block copolymers (PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA) with one block bearing primary/secondary hydroxyl groups and the second block with electroactive carbazole or fluorene moieties (Fig. 1). Interplay of hydrophilic and hydrophobic interaction leading to interesting self-assembled structures is expected. In addition, electropolymerization of carbazole or fluorene groups along the polymer backbone present on the hydrophobic block will lead to cross-CPN formation.

EXPERIMENTAL

Materials and Measurements

CuBr, CuCl, PMDETA, HMTETA, ethyl 2-bromoisobutyrate, and 9-hydroxy fluorene were purchased from Sigma Aldrich and used without further purification. Solketal, tosyl chloride, carbazole, 3-hydroxy benzyl alcohol, and methacryloyl chloride were purchased from Sigma-Aldrich and 18-crown ether-6 from Merck. ^{1}H and ^{13}C NMR spectra were recorded using Bruker ACF 300/AMX 500 MHz instrument. Molecular weight of polymers was determined by using gel permeation chromatograph (GPC, Shimadzu LC vt 10AT) instrument equipped with UV and refractive index detectors and polystyrene as standard. THF was used as an eluent at a flow rate of 0.3 mL/min. FT-IR spectra were recorded using Bio-Rad FT-IR spectrophotometer. Thermogravimetric analyses (TGA) were done on a TA-SDT2960 instrument using a heating rate of 10 °C/min under nitrogen atmosphere. The self-assembly

Additional Supporting Information may be found in the online version of this article.

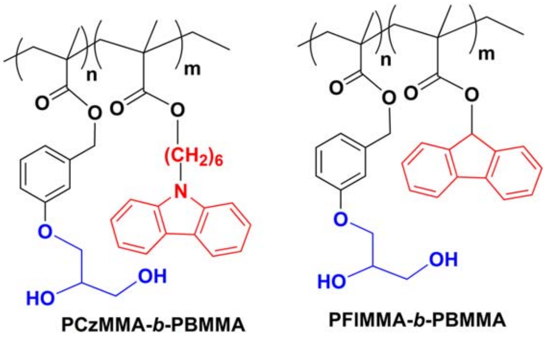


FIGURE 1 Molecular structure of target amphiphilic block copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

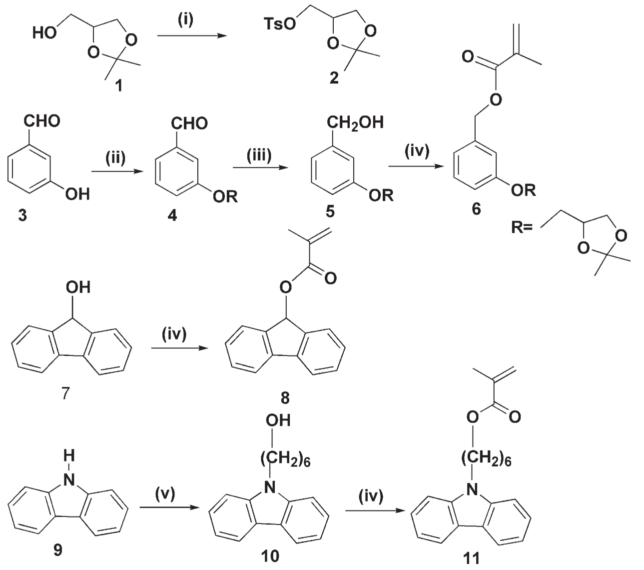
of block copolymers was investigated according to the following procedure. Deionized water (2 mL) was added dropwise to block copolymer solution in THF (2 mL, 0.05 mg/mL) under vigorous stirring. After 2 h, a drop of the dispersion was dried on a glass slide (Scanning electron micrograph, SEM) or carbon coated grid (TEM) and used for morphological studies. The morphology of the polymer in solid state was analyzed using JEOL 2010F at an accelerating voltage of 200 kV. SEM images were taken in JEOL JSM 6700 instrument. The wide angle X-ray scattering patterns were obtained using a D5005 Siemens X-ray diffractometer with Cu Kα (1.54 Å) radiation (40 kV, 40 mA). Sample was scanned between $2\theta = 2°$ and $50°$ with step size of $2\theta = 0.01°/\text{m}$. Cyclic voltammogram (CV) studies were performed using an Autolab PGSTAT30 Potentistat/Galvanostat with a standard three electrode electrochemical cell containing a 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at room temperature under nitrogen atmosphere using a scanning rate of 50 mV/s. A platinum/ITO working electrode, platinum counter electrode, and SCE (saturated KCl aqueous solution) reference electrode were used. Atomic force microscopy (AFM) imaging was done under ambient conditions with a PicoSPM II (PicoPlus, Molecular imaging) in the Magnetic AC mode (MAC mode). MAC mode uses a magnetic field to drive a magnetically coated cantilever in the top-down configuration.

Syntheses

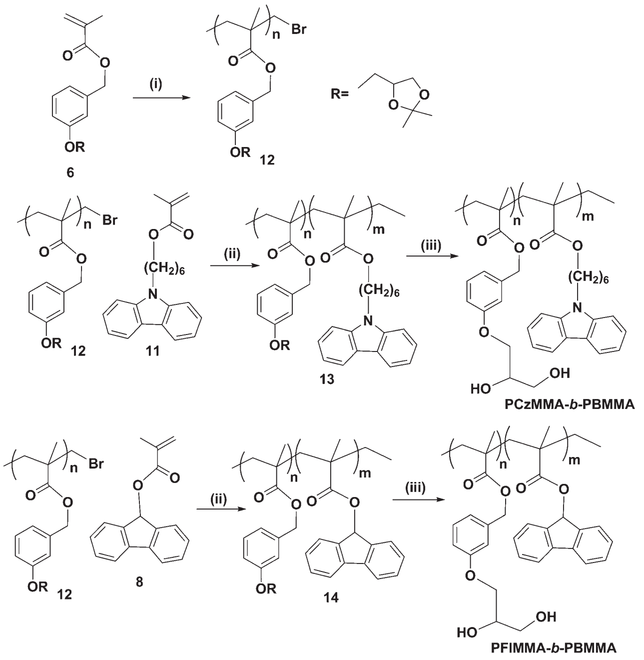
The primary synthetic goal was to synthesize amphiphilic methacrylate block copolymers from monomers functionalized with hydroxyl groups or electroactive groups. Block copolymers (PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA) were prepared using synthetic routes shown in Schemes 1 and 2. The monomers were synthesized by esterification reaction between hydroxyl group containing intermediates (5, 7, and 10) with methacryloyl chloride in dry THF and triethylamine at room temperature (Scheme 1).[23(c,d)]

Synthesis of (Toluene-4-sulfonic acid 2, 2-(dimethyl-[1, 3] dioxolan-4-ylmethyl ester) (2)

To a solution of solketal (15 g, 113 mmol) in THF (120 mL), a solution of NaOH (5N, 60 mL) was added. The contents were immersed in an ice bath and tosyl chloride (32.4 g, 170 mmol) in THF (100 mL) was added drop wise. The mixture was stirred overnight, concentrated, mixed with water, and extracted with ether. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated to give a low melting solid in quantitative yield (31 g, 98%). ^{1}H



SCHEME 1 Synthetic procedures for monomers: (i) p-TsCl, THF, 0 °C, 12 h; (ii) **2**, K_2CO_3, DMF, 18-crown-6, 75 °C, 5 days; (iii) THF/EtOH, $NaCNBH_3$, AcOH, rt, 12 h; (iv) methacryloyl chloride, triethylamine, THF, rt, 12 h; (v) KOH, DMSO, 1-bromohexanol, rt, 24 h.



SCHEME 2 Synthetic procedures: (i) CuBr/PMDETA, Ethyl 2-bromoisobutyrate, toluene, 75 °C; (ii) CuCl, HMTETA, anisole, 75 °C, 24 h; (iii) THF, 2M HCl, 70 °C, 2 h.

NMR (300 MHz, $CDCl_3$, δ ppm): 1.33 (s, 3H, —CH_3), 1.3 (s, 3H, —CH_3), 2.45 (s, 3H, Ar (—CH_3), 3.74 (m, 4H, —CH_2), 4.25 (m, 1H, —CH), 7.33 (d, 2H, J = 8.04Hz, Ar—H) 7.78 (d, 2H, J = 8.43 Hz, Ar—H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 145.0 (Ar—C—SO_2—), 132.4, 129.8, 127.8 (Ar—C), 109.9 (—C—), 72.7 (—CH), 70.6 (—CH_2), 65.9 (—CH_2), 30.7 (—CH_3), 26.4 (—CH_3), 24.9, 21.4 (—CH_3). MS-ESI: 287.1 (M + 1). ELEM. ANAL cal. $C_{13}H_{18}O_5S$: C, 54.53; H, 6.34; S, 11.20. Found: C, 54.47; H, 6.28; S, 11.14.

Synthesis of ([3-(2,2-Dimethyl-[1, 3] dioxolan-4-ylmethoxy)-phenyl]-methanol) (4)

Compound **3** (6.88 g, 56 mmol), potassium carbonate (23.5 g, 170 mmol), catalytic amount of 18-crown- 6, and DMF (120 mL) were mixed to get slurry. The reaction mixture was heated to 60 °C for 1 h under nitrogen atmosphere. Compound **2** (24 g, 83.8 mmol) in dry DMF (100 mL) was added drop wise in 30 min and the temperature was maintained at 75 °C for 5 days. The remaining K_2CO_3 was filtered off and the filtrate was poured into 1 L water and extracted with diethyl ether (3 × 50 mL). The organic layer was washed with water (3 × 50 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give a brown colored crude product. The compound was purified using flash silica column chromatography using hexane and ethyl acetate as eluent (7:3 v/v) to give compound **4** as colorless solid (10.3 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.39 (s, 3H, —CH_3), 1.41 (s, 3H, —CH_3), 3.86 (s, 2H, —CH_2), 4.40 (m, 1H, —CH), 4.08 (d, 2H, —CH_2—O), 6.88 (s, 1H, Ar—H), 7.32–7.37 (m, 3H, Ar—H), 10.01 (m, 1H, Ar—CHO). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 190.1, 158.5, 141.7, 129.6, 121.3, 113.4, 112.6 (Ar—C), 109.6, 77.8 (—CH—), 66.4 (—CH_2—), 64.2 (—CH_2—), 26.5 (—CH_3), 25.1 (—CH_3). FT-IR (cm^{-1}): 3255, 2987, 2872, 1605, 1491, 1370, 1151, 1091, 973, 842, 787, 694. MS-ESI (M + 1): 237.1. ELEM ANAL cal. $C_{13}H_{16}O_4$: C, 66.09; H, 6.83; Found: C, 66.12; H, 6.81.

Synthesis of ([3-(2,2-Dimethyl-[1, 3] dioxolan-4-ylmethoxy)-phenyl]-methanol) (5)

Compound **4** (8.5 g, 36 mmol) was dissolved in a mixture of THF/EtOH (70 mL: 25 mL) and cooled to 0 °C. Sodium cyanoborohydride (3.85 g, 62 mmol) was added at 0 °C followed by the addition of acetic acid (4.5 g, 75 mmol). The reaction mixture was stirred at room temperature for 12 h. $NaHCO_3$ solution (2M, 50 mL) was added slowly to it and product was extracted in diethyl ether (2 × 50 mL). The organic layer was washed with water (2 × 50 mL) and dried over anhydrous sodium sulfate. Filtered and concentrated under reduced pressure to give compound **5** in quantitative yield and used without further purification (4.75 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.37 (s, 3H, —CH_3), 1.43 (s, 3H, —CH_3), 3.83 (m, 4H, —CH_2), 4.40 (m, 1H, —CH), 4.59 (s, 2H, —CH_2OH), 6.78 (m, 1H, Ar—H), 6.89 (m, 2H, Ar—H), 7.19 (m, 1H, Ar—H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 158.5, 142.7, 129.3, 119.3, 113.4, 112.6 (Ar—C), 109.6 (—C—), 73.8 (—CH—), 68.4 (—CH_2OH), 66.4 (—CH_2—), 64.2 (—CH_2—), 26.5 (—CH_3), 25.1 (—CH_3). FT-IR (cm^{-1}): 3255, 2987, 2872, 1605, 1491, 1370, 1151, 1091, 973, 842, 787, 694. MS-ESI (M + 1): 239.12; ELEM. ANAL cal. $C_{13}H_{18}O_4$: C, 65.53; H, 7.61; Found: C, 65.49; H, 7.63.

Synthesis of (2-Methyl-acrylic acid 3-(2, 2-dimethyl-[1, 3] dioxolan-4-ylmethoxy)-benzyl ester) (6)

Compound **5** (2.5 g, 10.5 mmol) was dissolved in dry THF (25 mL). To the solution, triethylamine (2 g, 21 mmol) was added and cooled to 0 °C in an ice bath. Methacryloyl chloride (2.2 g, 21 mmol) dissolved in dry THF (15 mL) was added drop wise and stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was extracted using diethyl ether (3 × 50 mL). The organic layer was washed with $NaHCO_3$ solution (2N, 3 × 50 mL) and combined organic layers were dried over anhydrous sodium sulfate. Filtered and concentrated under reduced pressure to give the crude compound **6**. The product was purified using column chromatography on silica gel and hexane: ethyl acetate (8:2, v/v) mixture as eluent. The compound **6** was obtained as colorless oil (2.2 g, 68%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.40 (s, 3H, —CH_3), 1.46 (s, 3H, —CH_3), 1.81 (s, 3H, —CH_3), 3.86 (m, 4H, —CH_2), 4.14 (m, 1H, —CH), 5.15 (s, 2H, —CH_2O), 5.58 (s, 1H, =CH), 6.15 (s, 1H, =CH), 6.85 (m, 3H, Ar—H), 7.24 (m, 1H, Ar—H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 167.0 (C=O), 158.6, 137.6 (—C=CH_2), 136.0, 129.5, 125.7 (=CH_2), 120.5, 114.0, 109.6 (Ar—C), 103.4 (—C—), 73.8 (—CH), 68.6 (—CH2—O), 66.6 (—CH_2), 66.0 (—CH_2), 26.6 (CH_3), 25.2 (CH_3), 17.8 (CH_3). FT-IR (KBr, cm^{-1}): 2986, 1726, 1678, 1635, 1587, 1491, 1449, 1372, 1040, 943, 844, 783, 695. MS-ESI: 307.15 (M+1). ELEM. ANAL cal. $C_{17}H_{22}O_5$: C, 66.65; H, 7.24; Found: C, 66.59; H, 7.23.

Synthesis of Macroinitiator PBMMA-Br (12)

Compound **6** (0.96 g, 3.1 mmol) in toluene (10 mL) was transferred to a Schlenk flask and purged with nitrogen for 15 min. To the solution, CuBr (0.004 g, 0.027 mmol), and PMDETA (0.009 g, 0.052 mmol) were added. The solution was degassed three times, ethyl 2-bromoisobutyrate (0.098 g, 0.5 mmol) was added and mixture was heated to 75 °C. At different intervals of polymerization, the samples were taken, diluted with THF and injected into GPC for molecular weight determination. The final polymer was precipitated from large amount of hexane, filtered and dried. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.32 (s, 3H, —CH_3), 1.42 (s, 3H, —CH_3), 1.82 (3H, —CH3), 3.83 (m, 4H, —CH_2), 4.15 (broad, 1H, —CH), 4.47 (broad, 2H, —CH_2O), 6.81 (broad 1H, Ar—H), 6.97 (broad, 2H, Ar—H), 7.12 (broad, 1H, Ar—H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 158.5, 142.7, 129.3, 119.3, 113.4, 112.6 (Ar—C), 109.6 (—C—), 73.8 (—CH—), 68.4 (—CH_2OH), 66.4 (—CH_2—), 64.2 (—CH_2—), 26.5 (—CH_3), 25.1 (—CH_3). FT-IR (cm^{-1}): 2934, 2881, 1728, 1587, 1491, 1451, 1371, 1269, 1157, 1049, 930, 851, 783, 692. GPC (THF, PS standard): M_n = 6600 (M_w/ M_n = 1.12). ELEM. ANAL cal. $C_{19}H_{27}BrO_5$: C, 54. 95; H, 6.55; Found: C, 55.01; H, 6.63.

General Procedure for Synthesis of Precursor Polymers (13 and 14)

Macro-initiator **12** (0.2 g, 0.03 mmol) in anisole (10 ml) was transferred to a Schlenk flask and purged nitrogen for

30 min. CuCl (0.004 g, 0.03 mmol) and PMDETA (0.12 g, 0.6 mmol) were added to the flask. The flask was degassed and refilled with nitrogen three times using freeze-pump-thaw cycles. Nitrogen purged monomer **11** or **8** (0.03 mmol) was added to the Schlenk tube with macroinitiator, which was preheated in oil bath at 75 °C. Polymerization was carried out for 24 h and polymer **13** or **14** was precipitated from hexane, filtered, and dried to get a quantitative yield. The polymer was purified using re-precipitation method (three times) by dissolving in minimum amount of DCM, mixing with excess hexane, and centrifuged. The polymer was dried in vacuum oven at 60 °C for 1 day, before characterization.

Block Copolymer 13

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.87 (t, 3H, —CH_3), 1.25 (broad, 2H, —CH_2), 1.43 (s, 1H, —CH—), 1.70 (b, 2H, $\text{—CH}_2\text{—CH}_2\text{—}$), 1.85 (b, 2H, —CH_2), 3.72 (s, 6H, —CH_3), 3.76 (broad, 2H, N—CH_2), 4.02 (broad, 2H, $\text{—CH}_2\text{—O—}$), 4.21 (b, 4H, O—CH_2), 6.97 (broad, 1H, Ar—H), 7.10 (b, 1H, Ar—H), 7.18 (broad, 1H, Ar—H), 7.41 (b, 4H, Cz—H), 8.07 (b, 2H, Cz—H); ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 206.2 (—C=O), 158.5, 142.7, 140.3, 129.3, 125.6, 125.2, 122.8, 119.3, 118.7, 113.4, 112.6 (Ar—C), 109.6 (—C—), 108.5, 73.7 (—CH—), 69.4 ($\text{—CH}_2\text{—O—}$), 67.4 ($\text{—O—CH}_2\text{—}$), 67.2 ($\text{—CH}_2\text{—}$), 64.5, 60.3 (—N—CH_2), 26.5 (—CH_3), 42.8, 30.6, 26.9, 25.1 (—CH_3), 25.5, 24.7, 18.1. ELEM. ANAL: calculated; C, 73.14; H, 7.67; N, 2.13; Found; C, 73.03; H, 7.71; N, 2.04.

Block Copolymer 14

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.88 (t, 3H, —CH_3), 1.25 (broad, 1H, —CH), 2.38 (broad, 6H, —CH_3), 5.0 (broad, 2H, —CH_2), 5.12 (broad, 2H, $\text{—CH}_2\text{—O}$), 6.89–7.22 (broad 5H, Ar—H), 7.46 (broad, 4H, Fl—H), 7.80 (broad, 2H, Fl—H); ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 206.8 (—C=O), 158.5, 142.7, 141.8, 129.3, 129.4, 127.8, 126.8, 125.9, 120.0, 119.3, 113.4, 112.6 (Ar—C), 109.6 (—C—), 75.4 (—CH—), 73.8 (—CH—), 68.4 ($\text{—CH}_2\text{OH}$), 66.4 ($\text{—CH}_2\text{—}$), 64.2 ($\text{—CH}_2\text{—}$), 26.5 (—CH_3), 25.1 (—CH_3), 18.4. ELEM. ANAL: Calculated; C, 73.53; H, 6.88; Found; C, 73.48; H, 6.91.

General Procedure for Synthesis of Hydroxylated Block Polymers

The protected precursor block copolymers (**13**/**14**) were dissolved in THF (10 mL). To the solution, 2 M HCl (2.5 mL) solutions were added and the reaction mixture stirred at 70 °C for 2 h. The mixture was cooled, concentrated, and precipitated from excess amount of hexane. The polymer was purified by dissolving in minimum amount of DCM, added excess hexane, and centrifuged. The solid was then filtered and dried. The corresponding block copolymers, PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA were afforded in good yield.

PCzMMA-b-PBMMA

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 0.87 (broad, 2H, —CH_2), 1.16 (s, 1H, —CH—), 1.70 (b, 2H, $\text{—CH}_2\text{—CH}_2\text{—}$), 1.80 (b, 2H, —CH_2), 2.16 (s, 3H, —CH_3), 3.84 (broad, 2H, N—CH_2), 4.03 (broad, 2H, $\text{—CH}_2\text{—O—}$), 4.23 (b, 4H, O—CH_2), 6.85 (broad, 1H, Ar—H), 7.04 (b, 1H, Ar—H), 7.18 (broad, 1H, Ar—H), 7.36 (b, 2H, Cz—H), 7.42 (b, 2H, Cz—H), 8.07 (b, 2H, Cz—H); ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 206.9 (—C=O), 158.5, 142.7, 140.3, 129.3, 125.6, 125.2, 122.8, 120.3, 118.7, 113.4, 112.6 (Ar—C), 108.2, (—C—), 64.8 ($\text{—CH}_2\text{—O—}$), 64.7 ($\text{—O—CH}_2\text{—}$), 64.5 ($\text{—CH}_2\text{—CH}_2\text{—}$) 60.3 ($\text{—N—CH}_2$), 44.8, 44.2, 31.9, 28.6, 26.8, 25.9, (—CH_2), 14.1, 14.0 (—CH_3). ELEM. ANAL: calculated; C, 72.24; H, 7.82; N, 2.22; Found; C, 72.13; H, 7.71; N, 2.14.

PFlMMA-b-PBMMA

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 0.88 (b, 1H, —CH—), 1.43–1.67 (b, 2H, $\text{—CH}_2\text{—}$), 2.04 (s, 3H, —CH_3), 5.05 (b, 2H, $\text{—O—CH}_2\text{—}$), 5.12 (broad, 2H, $\text{—CH}_2\text{—O}$), 6.54 (b, 1H, Fl—H_9), 6.95–7.16 (broad 5H, Ar—H), 7.46 (broad, 4H, Fl—H), 7.72 (broad, 2H, Fl—H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 206.9 (—C=O), 158.5, 142.7, 141.8, 129.3, 129.4, 127.8, 126.8, 125.9, 120.0, 119.3, 113.4, 112.6 (Ar—C), 109.6 (—C—), 75.4 ($\text{—CH}_{\text{Fl}}\text{—}$), 66.4 ($\text{—CH}_2\text{OH}$), 64.8 ($\text{—CH}_2\text{—}$), 64.2 ($\text{—CH}_2\text{—}$), 26.5 (—CH—), 18.4 ($\text{—CH}_3$). ELEM. ANAL: Calculated; C, 72.51; H, 7.01; Found; C, 73.48; H, 6.98.

RESULTS AND DISCUSSIONS

Design and Synthesis of Monomers and Diblock Copolymers

The amphiphilic block copolymers were prepared from hydrophilic (hydroxyl polymethacrylate) and hydrophobic (electroactive aromatic) monomers. We chose groups such as carbazole and fluorene as side chains because they undergo electropolymerization under suitable conditions to afford a conducting polymer network (CPN). Commercially available solketal was reacted with tosyl chloride to give the protected compound **2**. Reaction of compound **2** with 3-hydroxy benzaldehyde gave **4**, which were reduced to alcohol **5** with sodium cyanoborohydride. The methacrylate monomer **6, 8**, and **11** was prepared from the corresponding alcohols and methacryloyl chloride, in presence of triethylamine as a base in THF at room temperature. Macro-initiator **12** ($M_n = 6600$, $M_w/M_n = 1.12$) was obtained from homopolymerization of **6** using atom transfer radical polymerization (ATRP) using ethyl 2-bromoisobutyrate as the initiator and CuBr/PMDETA as the catalyst. The macro-initiator **12** was used to copolymerize the fluorenyl/carbazolyl methacrylate using ATRP method of polymerization to afford precursor block copolymers **13** and **14** (Scheme 2). The block copolymers were readily soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, and THF. Hydroxylated polymethacrylate block copolymers (PFlMMA-*b*-PBMMA and PCzMMA-*b*-PBMMA) were achieved by deprotection of the dioxalane groups (precursor polymers **13** or **14**) using 2M HCl solution in THF at 70 °C. The molecular weights of diblock copolymers were determined using GPC with polystyrene standards. The GPC curves of block copolymers (PFlMMA-*b*-PBMMA and PCzMMA-*b*-PBMMA) are shown in Figure 2 and data are summarized in Table 1.

The chemical structures of the block copolymers PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA were confirmed from ^{1}H NMR and FT-IR spectra. The representative ^{1}H NMR of block

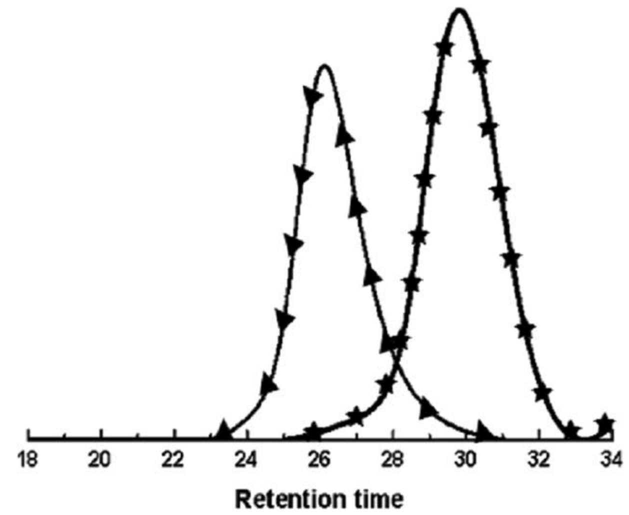


FIGURE 2 Gel Permeation Chromatography (GPC) plots of block copolymers: PFlMMA-*b*-PBMMA (▲) and PCzMMA-*b*-PBMMA (★) in THF against PS standards using a refractive index detector.

copolymers is shown in Figure S5 (see Supporting Information) and corresponding FT-IR spectra are shown in Figure S6 (see Supporting Information). Both copolymers contains a strong C═O stretching band at ~1724 cm^{-1} and a broad C—O band due to the ester group at ~1150 cm^{-1}. The sharp peak at 1250 cm^{-1} in the spectrum of PCzMMA-*b*-PBMMA shows N—C bond stretching, which is absent in the spectrum of PFlMMA-*b*-PBMMA. The molecular weights and physical properties of block copolymers are summarized in Table 1.

Photophysical Properties

The normalized absorption and emission spectra of PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA in THF are shown in Figure 3. The absorption band of PCzMMA-*b*-PBMMA below 350 nm is attributed to the absorption by the π-π^*, n-π^*, and benzenoid transitions of carbazole and phenyl groups. The absorption band of PFlMMA-*b*-PBMMA below 300 nm is attributed to the absorption by the π-π^*, n-π^* transitions of fluorene groups.[18] The block copolymers did not exhibit any new bands in the absorption spectra, indicating that there is no chemical changes in chromophores during the polymerization.

The emission spectra of the block copolymers are shown in Figure 3(b). The emission peaks at 353 and 366 nm for PCzMMA-*b*-PBMMA and 315 nm for PFlMMA-*b*-PBMMA indicates the emission from carbazole and fluorene groups, implying that the formation of intermolecular exciplex can be ruled out in solution. This supports the previous conclusion that the chromophores were not in the stacked form.[19] The UV–vis and fluorescence spectra of the corresponding homopolymers are shown in Supporting Information Figure S4.

TABLE 1 Physical Properties of Block Copolymers

Polymer	Hydrophobic group	[a]$M_n \times 10^3$	PDI[a]	Molar fraction Monomers	m:n (mol %)[b]	Decomposition Temperature (T_d; °C)[c]	Glass Transition Temperature (T_g; °C)[d]
PFlMMA-*b*-PBMMA	Fluorene	33	1.57	50.50	47:22	250	92
PCzMMA-*b*-PBMMA	Carbazole	22	1.17	50.50	36:12	337	51

[a] Determined from GPC (THF, Polystyrene standard).
[b] Monomers ratio present on block copolymers calculated from NMR.
[c] Determined from TGA curve (N_2 atmosphere, 10 °C/min scan rate).
[d] Determined from DSC (N_2 atmosphere, 5 °C/min scan rate).

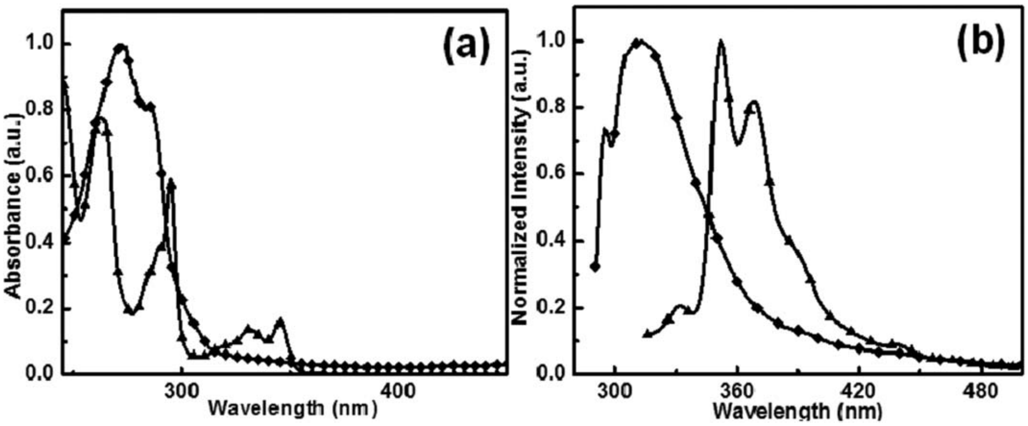


FIGURE 3 Absorption (a) and emission spectra (b: excitation at 290 nm) of PCzMMA-*b*-PBMMA (▲) and PFlMMA-*b*-PBMMA (◆) in THF.

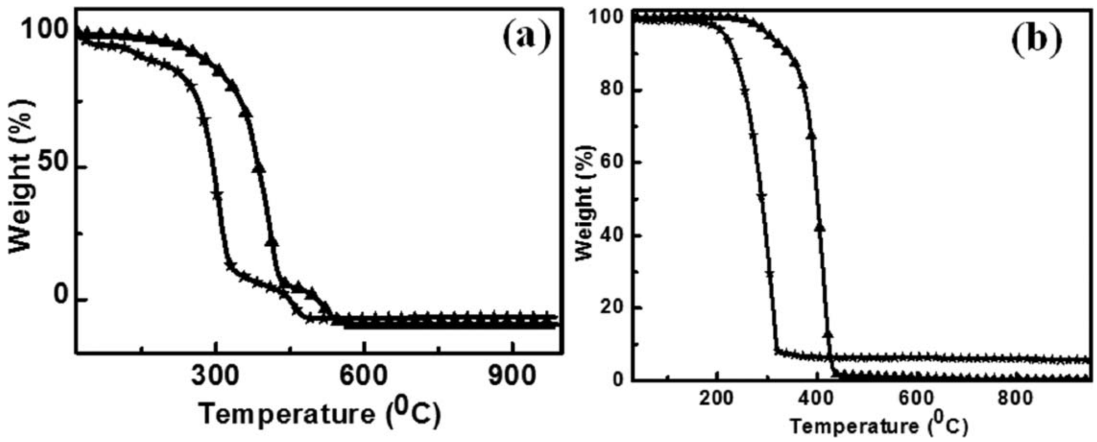


FIGURE 4 TGA of protected (a) and deprotected (b) block copolymers: PFlMMA-*b*-PBMMA (▲) and PCzMMA-*b*-PBMMA (★) in N_2 atmosphere with a heating rate of 10 °C/min.

Thermal Properties

The thermal properties of block copolymers were determined by TGA. Figure 4 represents the TGA curves of the deprotected and protected block copolymers under N_2 atmosphere. The hyroxylated copolymers (PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA) were stable up to 300 °C and showed only single stage decomposition. The observed thermal stability of a block copolymer bearing carbazole moiety can be explained by the presence of spacer linkage between the polymer backbone and the chromophore unit. It was noticed that the residual weights of the deprotected copolymers were reduced to zero in the TGA thermograms around 500 °C, indicating a complete degradation of the polymer chain [Fig. 5(b)]. The protected block copolymers (**13** and **14**) showed two degradation temperatures and stable up to 250 °C [Fig. 5(a)]. The glass transition temperature (T_g) of block copolymers PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA were 51 and 92 °C, respectively. The pendant groups tend to decrease the glass transition temperature of the block copolymers owing to disordered packing of bulky groups in the polymer lattice. The DSC curves for block copolymers are shown in Supporting Information Figure S3.

Morphology Studies of Block Copolymer Self-Assembly

The self-assembly of block copolymers was investigated using SEM and TEM. FE-SEM micrographs of block copolymers PCzMMA-*b*-PBMMA (a) and PFlMMA-*b*-PBMMA (b) are given in Figure 5. The micrographs show the formation of smooth nanorod structures for PCzMMA-*b*-PBMMA with a thickness of 90 nm on a glass surface. The block copolymer, PFlMMA-*b*-PBMMA formed vesicle type structure through self-assembly. The morphological characteristic was further examined using transmission electron microscopy (TEM). The TEM images of block copolymers are shown in Figure 5(c,d). The block copolymer, PCzMMA-*b*-PBMMA showed a lamella type packing along the nanorod (c) axis, in which black domains (hydrophilic) alternates with white domains (hydrophobic). Similarly, TEM image of block copolymer PFlMMA-*b*-PBMMA (d) showed vesicular assemblies with a membrane thickness of 30–80 nm. Considering that the polar block is same in both cases, such differences may be due to the subtle differences among carbazole and fluorene groups, where fluorene incorporated block induce more hydrophobicity than carbazole incorporated blocks.

Water is a good solvent for hydrophilic block (i.e., hydroxylated polymethacrylate), but a nonsolvent for hydrophobic block (i.e., carbazole or fluorene functionalized). In case of PCzMMA-*b*-PBMMA, the flexibility of long alkyl spacer, molecular dipole, and π–π stacking tends to play role in the formation of lamella morphology. In the case of block copolymer, PFlMMA-*b*-PBMMA, the hydrophobic fluorene groups are

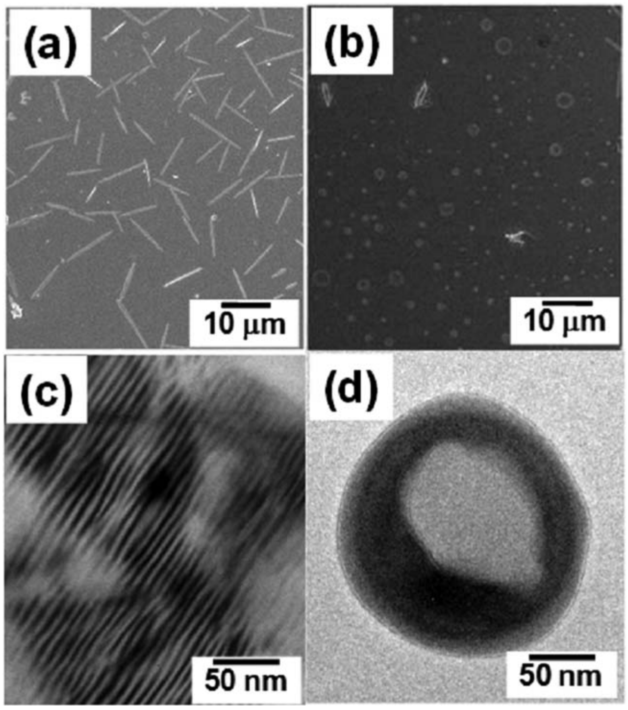


FIGURE 5 SEM (top) and TEM (bottom) images of block copolymers: PCzMMA-*b*-PBMMA (a, c) and PFlMMA-*b*-PBMMA (b, d) in THF: H_2O (1:1) with concentration of 0.05 mg/mL.

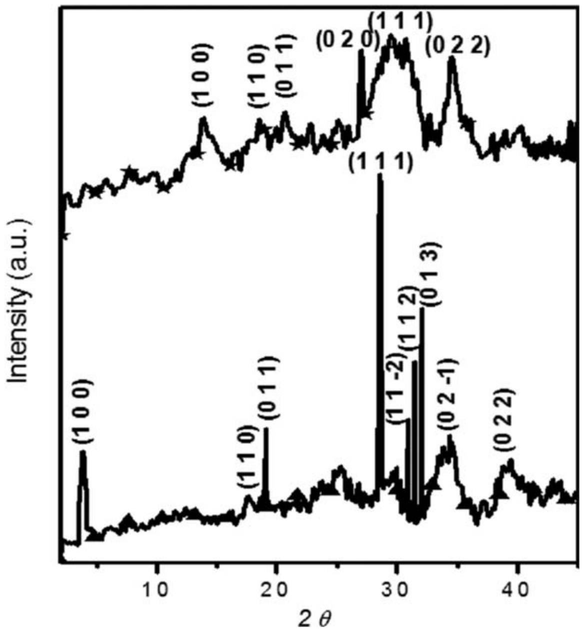


FIGURE 6 X-ray diffraction pattern of block copolymer thin films with step size of $2\theta = 0.01°$/m. PCzMMA-*b*-PBMMA (▲) and PFlMMA-*b*-PBMMA (★) on a glass slide.

directly connected to the backbone and more rigid and a bilayer structure would be preferred with hydrophilic block mixing with water phase. Formation of nanostructures for PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA was further confirmed using wide angle X-ray diffraction (WAX) experiment. The self-assembled solution of block copolymers was drop casted on a glass cover slip and dried at room temperature.

Figure 6 shows the X-ray diffraction pattern of PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA. PCzMMA-*b*-PBMMA results a diffraction peak at lower angle at $2\theta = 3.72°$ correspond to the thickness of lamella formed by the blocks. It shows a long-range order and sharp peak at $2\theta = 28.54°$ correspond to the *d*-spacing of 3.13 Å is close to the typical distance (~3.5 Å) for an effective $\pi - \pi$ stacking between the aromatic molecules.[26] In the diffraction pattern of PFlMMA-*b*-PBMMA, no low angle diffraction peaks were observed and broad diffraction peaks at high angle region at $2\theta = 29.35°$ correspond to *d*-spacing of 3.0 Å is close to an effective $\pi - \pi$ stacking between the aromatic molecules inside the bilayer structure of the vesicles.[24] The vesicles and lamella structure of block copolymers is schematically represented in Figure 7.

Electrochemical Polymerization

Electropolymerization of block copolymers was investigated using cyclic voltammetry with Ag/AgCl as reference electrode, platinum as counter electrode, ITO substrate as working electrode and tetrabutylammonium hexafluorophosphate (TBAP, 0.1 M) as supporting electrolyte. The block copolymers PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA solution (10 wt % in DCM) were spin coated onto ITO substrate and used for the electropolymerization at a scan rate of 50 mV/s.

Figure 8 shows the CV traces for the block copolymers PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA. No changes in peak positions or intensities in the polymer free scan shows that all polymerizable groups on the polymer backbone have been polymerized with no changes in peak intensities. For block copolymer PCzMMA-*b*-PBMMA, oxidation potential of the tethered carbazole monomer was observed at 0.9 V on the first cycle. Starting from second anodic scan, one new anodic peak at 1.05 V appeared with a reduction peak at

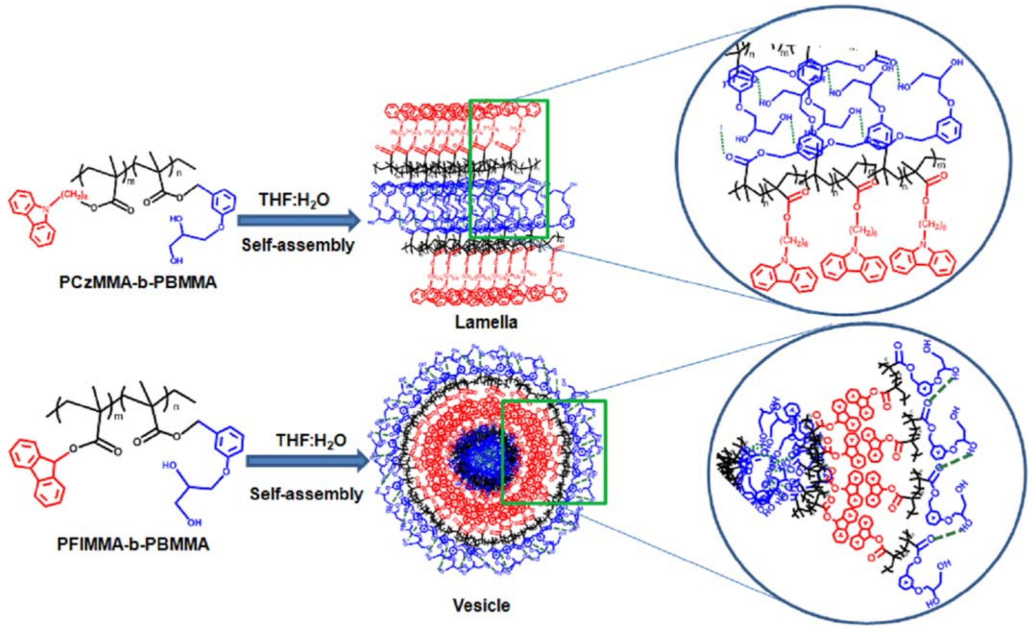


FIGURE 7 Schematic representation of lamella and vesicle structure formation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

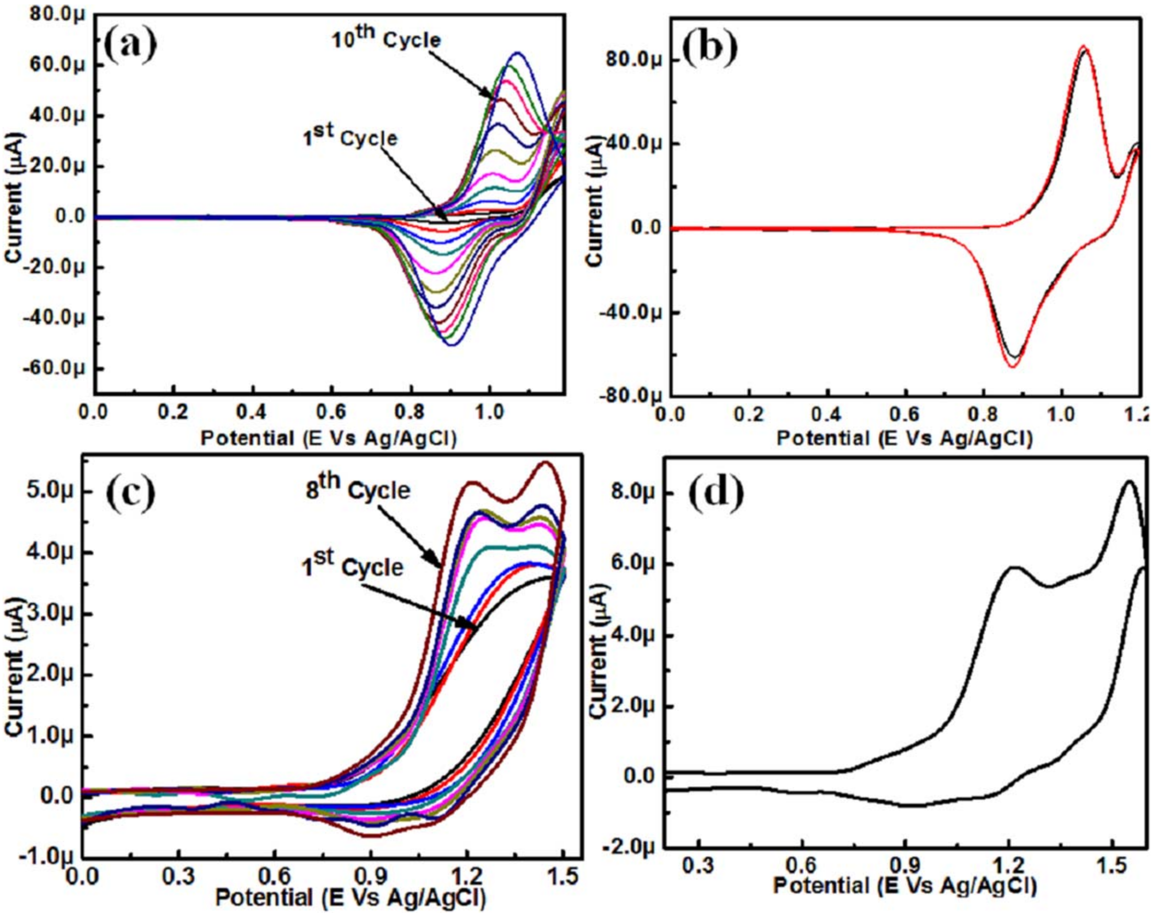


FIGURE 8 Ten cycle CV for electrochemical polymerization of block copolymers (a) PCzMMA-*b*-PBMMA, (c) PFlMMA-*b*-PBMMA. Polymer free scans for block copolymers after electropolymerization of PCzMMA-*b*-PBMMA (b) and PFlMMA-*b*-PBMMA (d). Tetrabutylammonium hexafluorophosphate (TBAP, 0.1M) is used as supporting electrolyte in acetonitrile. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.85 V, which corresponds to the radical cation of dimer unit [Fig. 8(a)].[22] Subsequent cycles showed the same onset values of oxidation and reduction peaks with increase in current values, suggesting the electropolymerization of carbazole unit. The polymer free scan [Fig. 8(b)] of the crosslinked polymer film shows complete electropolymerization of carbazole groups to form stable polycarbazole. The crosslinking mechanism of carbazole unit is explained in Supporting Information Figure S9.[27]

For PFlMMA-*b*-PBMMA, oxidation potential of the tethered fluorene monomer was at 1.24 V for the first three cycles. Starting from fourth anodic scan, two oxidation peaks (Epa1 and Epa2) appeared at 1.24 and 1.43 V and two reduction peaks (Epc1 and Epc2) at 0.9 and 1.10 V [Fig. 8(c)], which corresponds to the formation of radical cation and bication species of the dimer unit, respectively.[23] The anodic and cathodic peak potentials were increased in the subsequent cycles. The polymer free scan of crosslinked polymer film showed the redox potential peaks [Fig. 8(d)] with no changes in repeated scans.[23] This confirms complete polymerization of fluorene groups to form a CPN of polyfluorene inside the polymer lattice. Crosslinked polymer network formation was further confirmed from the linear relationship between the current and the number of scans for both polymers [Fig. 9(a,b)] which shows increase in current with number of scans.

The electropolymerized thin films on ITO substrate were further characterized by UV–vis, fluorescence, FT-IR spectroscopy, and AFM measurements. The UV–vis spectra of crosslinked film of PCzMMA-*b*-PBMMA and PFlMMA-*b*-PBMMA showed an absorption maximum at higher wavelength compared to the precursor. This confirms the formation of conjugated polymer chain through electropolymerization of electroactive units. For block copolymer PCzMMA-*b*-PBMMA [Fig. 10(a)], the absorption peak at 300 nm wavelength can be assigned as polaron bonding to π^* conduction band and the 520 nm peak appears due to transition in bonding to antibonding state i.e. π - π^* transition.[25] However, for block copolymer PFlMMA-*b*-PBMMA [Fig. 10(c)], the observed red shift of absorption peak at 320 nm indicates an extended conjugation along the polymer chain. The emission spectra of the electropolymerized films showed

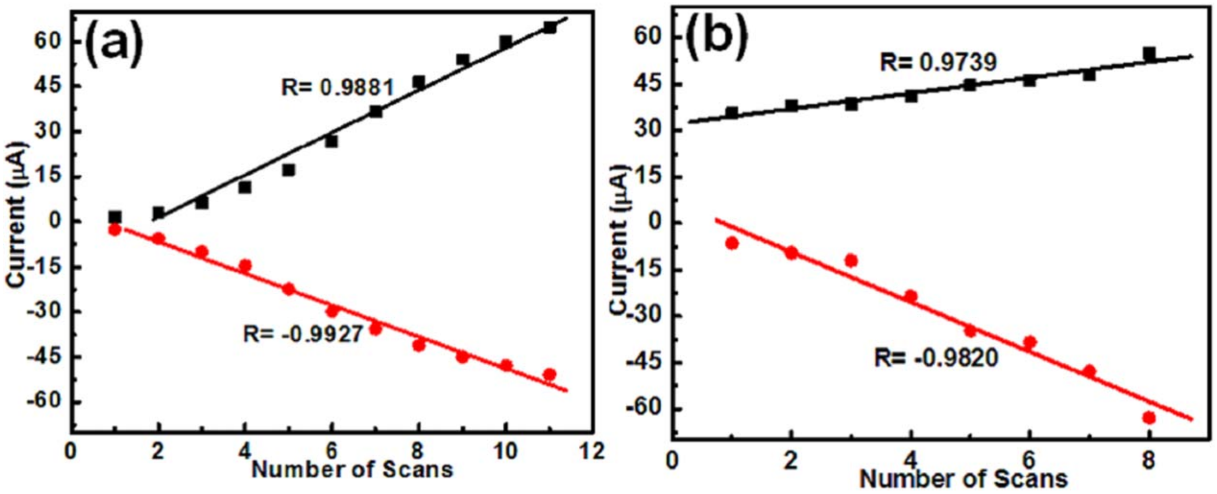


FIGURE 9 Linearity of current with number of scans of electropolymerization of block copolymers: (a) PCzMMA-*b*-PBMMA and (b) PFlMMA-*b*-PBMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

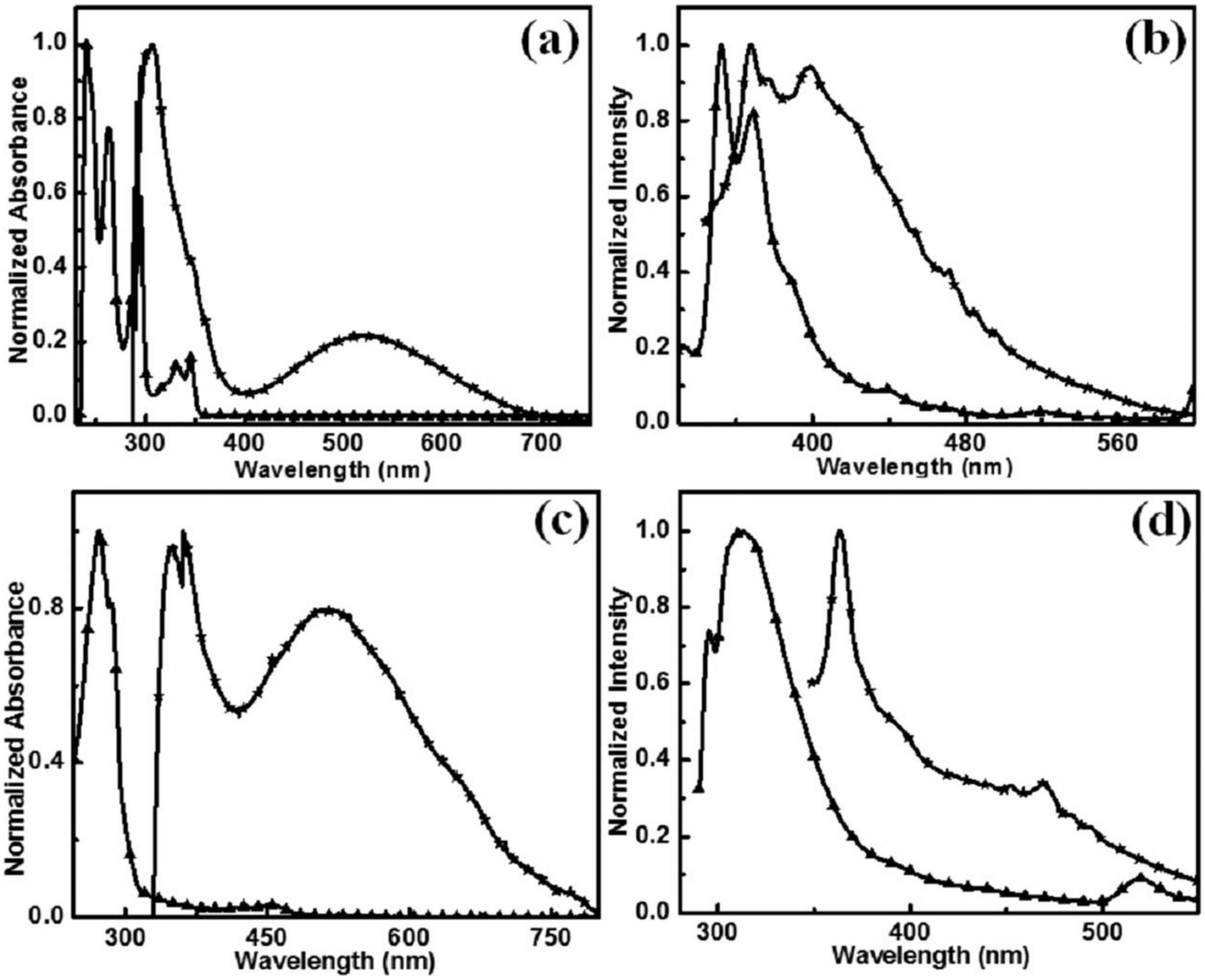


FIGURE 10 Absorption (a, c) and emission (b, d) spectra of electropolymerized films on ITO with its precursor block copolymers PCzMMA-*b*-PBMMA (a, b) and PFlMMA-*b*-PBMMA (c, d); Precursor polymer (▲) and electropolymerized film (★).

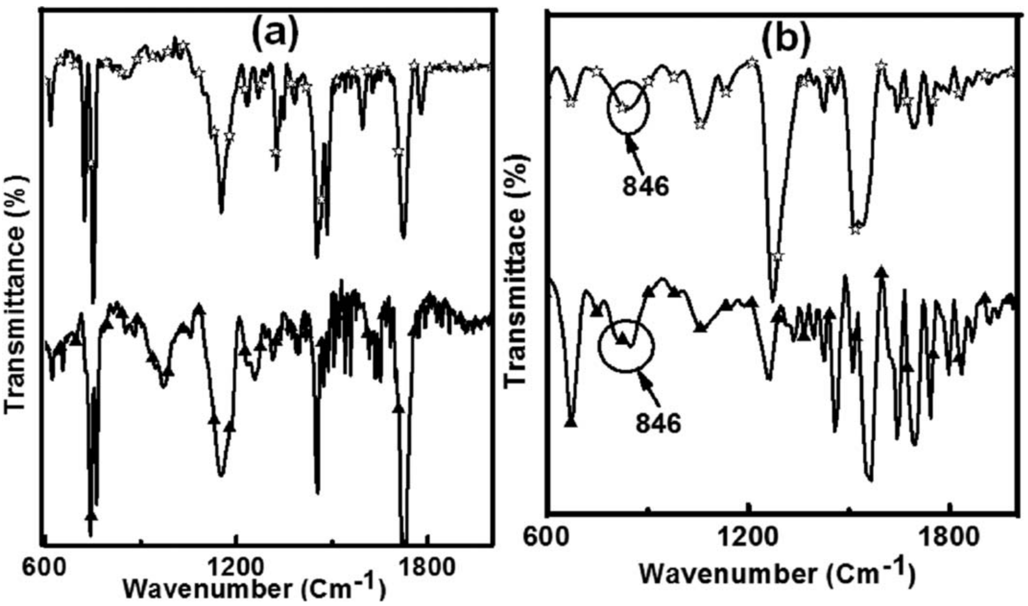


FIGURE 11 FT-IR spectra of block copolymers; precursor polymer (a) and after electropolymerization (b); PCzMMA-*b*-PBMMA (▲) and PFlMMA-*b*-PBMMA (☆). The spectra were recorded in KBr matrix at R.T.

red shift compared to the precursor polymers [Fig. 10(b,d)]. The electropolymerized polymers showed the appearance of extra peaks due to polymer formation in the FT-IR spectrum at 846 cm^{-1} [Fig. 11(b)], which is absent for precursor polymer [Fig. 11(a)] and corresponds to the C—H out- of- plane bending vibrations of 1, 2, 3, 4-substituted aromatic units.[26]

The electropolymerization of electroactive units to form a polymer film was also monitored with different number of scans at a scan rate of 50 mV/s. The absorption peaks at lower (300 nm) and higher (520 nm) wave lengths in the absorption spectra showed a linear increase with increase in number of CV cycles leads the formation of longer polymer chains [Supporting Information Fig. S7(a,b)]. As expected, polymerization of carbazole groups was much faster than the fluorene groups. The calculated band gaps for electropolymerized block copolymers were 1.76 eV (PCzMMA-*b*-PBMMA) and 1.64 eV (PFlMMA-*b*-PBMMA). The surface morphology and molecular orientation of crosslinked films on ITO substrate was studied using AFM.[22] Polymerized PCzMMA-*b*-PBMMA film showed sheets stacked layers with 250 nm length and 100 nm of width with an interlayer separation of 3.5 nm and formed large crystals (Supporting Information Fig. S8). However, for polymerized PFlMMA-*b*-PBMMA block copolymer film showed ring like nanostructures [Supporting Information Fig. S8(b)]. These rings were of 25 nm in thickness and 80–100 nm internal diameters. The observed dimensions are complimentary to the data collected from TEM images of nonpolymerized self-assembled structures.

CONCLUSIONS

In this study, methacrylate monomers functionalized with fluorine, carbazole, and 2,2-dimethyl-1,3-dioxolane were prepared and polymerized using ATRP to form diblock copolymers with hydrophobic and hydrophilic blocks. The macroinitiator (PBMMA-Br) was synthesized from 2,2-dimethyl-1,3-dioxolane functionalized methacrylate monomer. The carbazole incorporated block copolymer formed lamella, while fluorene incorporated copolymer showed vesicle morphologies via self-assembly in solution. The interplay of weak interactions such as hydrogen bonding and van der Wall's interactions are responsible for the formation of nanostructures from these block copolymers. A range of spectroscopic and electron microscopic techniques were used to characterize the structure and properties of the polymers. The cyclic voltammetry and AFM were used to electropolymerize the carbazole and fluorene groups to from CPN inside the polymer lattice.

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REFERENCES AND NOTES

1 (a) Q. Huibin, D. Van An, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2013**, *135*, 17739; (b) E. Lejeune, M. Drechsler, J. Jestin, A. H. E. Müller, Ch. Chassenieux, O. Colombani, *Macromolecules* **2010**, *43*, 2667; (c) E. S. Savariar, S. V. Aathimanikandan, S. Thyumanavan, *J. Am. Chem. Soc.* **2006**, *128*, 16224–16230.

2 R. Savic, L. B. Luo, A. Eisenberg, *Science* **2003**, *300*, 615.

3 (a) M. Antonietti, S. Forster, *Adv. Mater.* **2003**, *15*, 1323–1333; (b) M. Sarikaya, C. Tamerler, A. K. Y. Jen, K. Schulten, F. Baneyx, *Nature Mater.* **2003**, *2*, 577–585.

4 (a) D. Sundrani, S. B. Darling, S. J. Sibener, *Nano Lett.* **2004**, *4*, 273; (b) K. W. Guarini, C. T. Black, S. H. I. Yeung, *Adv. Mater.* **2002**, *14*, 1290.

5 (a) L. Zhang, K. Yu, A. Eisenberg, *Science* **1996**, *232*, 1777; (b) S. A. Jenekhe, K. L. Chen, *Science* **1999**, *283*, 372.

6 (a) D. W. P. M. Loewik, J. C. M. van Hest, *Chem. Soc. Rev.* **2004**, *33*, 234–245; (b) E.-H. Ryu, Y. Zhao, *Org. Lett.* **2004**, *6*, 3187–3189.

7 (a) S. H. Kim, M. J. Minser, T. Xu, M. Kimura, T. P. Russell, *Adv. Mater.* **2004**, *16*, 226; (b) M. C. Stuparu, A. Khan, C. J. Hawker, *Polym. Chem.* **2012**, *3*, 3033.

8 (a) S. Choi, E. Kim, H. Ahn, S. Naidu, Y. Lee, D. Y. Ryu, C. J. Hawker, T. P. Russell, *Soft Matter* **2012**, *8*, 3463; (b) R. A. Segalman, A. Hexemer, E. J. Kramer, *Macromolecules* **2003**, *36*, 6831.

9 (a) K. Aissou, A. Pfaff, C. Giacomelli, Ch. Travelet, A. H. E. Müller, R. Borsali, *Macromol. Rapid Commun.* **2011** *32*, 912; (b) G.-D. Liang, J.-T. Xu, Z.-Q. Fan, S.-M. Mai, A. J. Ryan, *Polymer* **2007**, *48*, 7201–7210.

10 (a) K. Kempe, K.L. Killops, J.E. Poelma, H.J. Jung, J. Bang, R. Hoogenboom, H. Tran, C.J. Hawker, U.S. Schubert, L.M. Campos, *ACS Macro Lett.* **2013**, *2*, 677; (b) M. Shah, V. Pryarnitsyn, V. Ganesan, *Macromolecules* **2008**, *41*, 218–229.

11 (a) A. M. Atta, K.-F. Arndt, *Polym. Int.* **2005**, *54*, 448; (b) S. J. Kim, S. J. Park, I. Y. Kim, T. D. Chung, H. C. Kim, S. I. J. Kim, *Appl. Polym. Sci.* **2003**, *90*, 881–885; (c) S. J. Kim, S. G. Yoon, Y. M. Lee, K. H. An, S. I. J. Kim, *Appl. Polym. Sci.* **2003**, *90*, 1389–1392.

12 (a) K. Kataoka, A. Harada, Y. Nagasaki, *Adv. Drug Delivery Rev.* **2001**, *47*, 113.

13 F. Simal, M. Jeusette, P. Leclerec, *J. Adhes. Sci. Tech.* **2007**, *21*, 559–574.

14 (a) P. Yang, M. Yang, S. L. Zou, *J. Am. Chem. Soc.* **2007**, *129*, 1541–1552; (b) S. Biggs, K. Sakai, T. Addison, A. Schmid, S. P. Armes, M. Vamvakaki, V. Bütün, G. Webber, *Adv. Mater.* **2007**, *19*, 274–250.

15 G.-D. Liang, J.-T. Xu, Z.-Q. Fan, S.-M. Mai, A. J. Ryan, *Polymer* **2007**, *48*, 7201–7210.

16 W. Lee, C. F. Chen, *Polym. Gels Netw.* **1998**, *6*, 439.

17 G. Riess, *Prog. Polym. Sci.* **2003**, *28*, 1107–1170.

18 (a) S. Jain, F. S. Bates, *Macromolecules* **2004**, *37*, 1511–1523; (b) P. Lim Soo, A. Eisenberg, *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 923–938.

19 H. Kaya, L. Willmer, J. Allgaier, J. Stellbrink, D. Richter, *Appl. Phys. A: Mater. Sci. Process* **2002**, *74*, 499–501.

20 (a) S. A. Jenekhe, K. L. Chen, *Science* **1998**, *279*, 1903; (b) X. Kong, S. A. Lenekhe, *Macromolecules* **2004**, *37*, 8180.

21 Z. R. Zhang, G. J. Liu, S. Bell *Macromolecules* **2000**, *33*, 7877; (b) M. Save, J. V. M. Weaver, S. P. Armes, *Macromolecules* **2002**, *35*, 1152.

22 (a) X. L. Chen, S. A. Jenekhe, *Langmuir* **1999**, *15*, 8007; (b) R. S. Meissner, J. Rebek, de Mendoza, *Science* **1995**, *270*, 1485–1488; (c) L. F. Zhang, C. Bartels, Y. S. Yu, H. W. Shen, A. Eisenberg, *Phys. Rev. Lett.* **1997**, *79*, 5034–5037.

23 (a) R. Ravindranath, P. K. Ajikumar, S. Bahulayan, A. Baba, R. C. Advincula, W. Knoll, S. Valiyaveettil, *J. Phys. Chem. B.* **2007**, *111*, 6336–6343; (b) S. Deng, R. C. Advincula, *Chem. Mater.* **2002**, *14*, 4073–4080; (c) S. Inaoka, R. C. Advincula, *Macromolecules* **2002**, *35*, 1426–1428; (d) P. Taranekar, A. Baba, T. M. Fulghum, R. Advincula, *Macromolecules* **2005**, *38*, 3679–3687.

24 (a) A. A. Rafati, A. R. A. Borujeni, M. Najafi, A. Bagheri, *Mater. Charact.* **2010**, *62*, 94–98; (b) H. Wang, X. Zheng, P. Chen, X. Zheng, *J. Mater. Chem.* **2006**, *16*, 4701–4705.

25 (a) Z. Li, G. J. Liu, *Langmuir* **2003**, *19*, 10480; (b), Y. Z. Jin, C. Gao, H. W. Kroto, T. Maekawa, *Macromol. Rapid Commun.* **2005**, *26*, 1133–1139; (c) C. Granel, P. Dubois, R. Jerome, P. Teyssie, *Macromolecules* **1996**, *29*, 8576.

26 (a) J. Guay, R. Dao, L. H. Paynter, *Macromolecules* **1990**, *23*, 3598–3605; (b) W. Kemp, Organic Spectroscopy; Palgrave: New York, **1991**; (c) D. L. Pavia, M. Lampman, G. S. Kriz, Introduction to Spectroscopy: A Guide for Students of Organic Chemistry; Saunders: Philadelpha, **1979**.

27 (a) S. Barik, S. Valiyaveettil, *Macromolecules*, **2008**, *41*, 6376–6386; (b) S. Jagadesan, S. Sindhu, R. C. Advincula, S. Valiyaveettil, *Langmuir* **2006**, *22*, 780–786; (c) S. Jegadesan, S. Sindhu, S. Valiyaveettil, *Small* **2006**, *2*, 481–484; (d) S. Jagedesan, P. Taranekar, S. Sindhu, R. C. Advinclula, S. Valiyaveettil, *Langmuir* **2006**, *22*, 3807–3811.