# Synthesis, structures and multifunctional sensory properties of poly[2,7-(9,9-dihexylfluorene)]-*block*-poly[2-(dimethylamino)ethyl methacrylate] rod-coil diblock copolymers<sup>†</sup>

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The synthesis, structures and multifunctional sensory properties of amphiphilic poly[2,7-(9,9dihexylfluorene)]-block-poly[2-(dimethylamino)ethyl methacrylate] (PF-b-PDMAEMA) rod-coil diblock copolymers are reported. The new copolymers, with PDMAEMA coil lengths of 31, 45, 93 and 185 repeating units, were synthesized by atom transfer radical polymerization. The surface structures and photophysical properties of the synthesized polymers were studied through the variation of solvent composition (water-THF), temperature, and pH. The PF7-b-PDMAEMA45 structure changed from spheres to separate cylinders, bundles of cylinders and spiral-shaped micelles as the solvent composition changed from 0 to 90 wt% water in THF. However, the long-range order structure of spiral-shaped loops was not observed at a long coil length. The micellar aggregates of PF7-b-PDMAEMA45 in water showed a reversible surface structure transformation from cylinder-bundles to spheres on heating from 25 to 75 °C. The variation of the micelle size with temperature was judged to be similar from both atomic force microscopy (AFM) and dynamic light scattering (DLS) measurements. The intermolecular PF aggregations led to fluorescence quenching and a blue-shift in the absorption spectra of the block copolymer as the water content increased. The photoluminescence (PL) intensity of  $PF_7$ -b-PDMAEMA<sub>45</sub> in water was thermoreversible based on its lower critical solution temperature. The PL characteristics suggested the new copolymers behave as an on/off fluorescence indicator of temperature or pH, with a reversible "on-off" profile at an elevated temperature in water: the pH-fluorescence intensity profile switched from "off-on" to "on-off" as the temperature increased. The present study suggests that PF-b-PDMAEMA copolymers have potential applications as multifunctional sensory materials toward solvent, temperature, and pH.

## Introduction

Self-assembly of  $\pi$ -conjugated-based rod-coil block copolymers has been demonstrated as a powerful route towards supramolecular objects with novel architectures, functions and physical properties.<sup>1-3</sup> Aggregation and microphase separation of such block copolymers could yield various nanoscale morphologies with novel functionalities driven by the solvent selectivity or the  $\pi$ - $\pi$  interaction of the rigid segments.<sup>4,5</sup>

Different conjugated moieties of  $\pi$ -conjugated rod-coil block copolymers have been reported in the literature, including thiophene,<sup>6</sup> phenylene,<sup>7</sup> quinoline,<sup>8</sup> and fluorene.<sup>9</sup> We are particularly interested in fluorene-based rod-coil block copolymers due to their high thermal/chemical stability and excellent fluorescence quantum yields.<sup>10</sup> The incorporation of coil segments into the polyfluorene backbones could not only allow manipulation of the electronic and optoelectronic properties, but could also generate self-assembling nanostructures, such as spheres, nanoribbons, honeycombs or worm-like structures.<sup>9b-e</sup> In addition, the combination of a stimuli-responsive coil segment<sup>9b,11</sup> with the tunable photophysical properties of a  $\pi$ -conjugated rod could produce novel multifunctional sensory materials. Bo and coworkers<sup>11a</sup> reported a functional coil-rodcoil triblock copolymer containing a terfluorene rod segment and poly(*N*-isopropylacryamide) (PNIPAAm). Such block copolymers showed the morphological transformation of coil to collapsed globular structure at the lower critical solution temperature (LCST) and significant changes of the fluorescence characteristics by blending in tetraphenylporphine tetrasulfonic acid.

We have discovered new copolymers consisting of a PNI-PAAm block and a fluorescent difluorene-containing acrylic polymer block with both a pH-response and DNA-sensing ability.<sup>11d</sup> Recently, a significant variation in the surface structure and photophysical properties of fluorene-coil block copolymer brushes toward environmental stimuli was also reported by our group.<sup>96</sup>

Poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) has both temperature- and pH-responsive characteristics.<sup>12</sup> PDMAEMA based coil-coil block copolymers exhibited tunable micelle morphology with potential biological applications.<sup>13</sup> The

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aggregate formation of PDMAEMA-polyfluorene-PDMAEMA coil-rod-coil copolymers in a water–THF solvent system resulted in the formation of excimers and reduced quantum efficiency.<sup>9/</sup> Nevertheless, the detailed structures and photophysical properties of rod-coil diblock copolymers with multifunctional sensory characteristics requires further exploration.

In this paper, the synthesis, structures and multifunctional sensory properties of amphiphilic poly[2,7-(9,9-dihexylfluorene)]*b*-poly[2-(dimethylamino)ethyl methacrylate] (PF-*b*-PDMAEMA) rod-coil diblock copolymers are reported. PF-b-PDMAEMA copolymers with four different block lengths were synthesized by atom transfer radical polymerization, as shown in Scheme 1. The surface structures and photophysical properties of the synthesized polymers were studied through the variation of solvent composition (water-THF), temperature, and pH. The aggregate micelles were characterized by atomic force microscopy (AFM). The photophysical properties of the prepared block copolymers in solution were characterized by optical absorption and photoluminescence (PL). The AFM surface structures and photophysical properties were correlated with rod/coil block ratios and stimuli parameters. The experimental results suggest that PF-b-PDMAEMA copolymers have significant variation on the surface structures and fluorescence characteristics toward solvent, temperature, and pH.

## Experimental

#### Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA, Acros, 99%), was passed through an  $Al_2O_3$  column prior to polymerization. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA, Acros, 99%), was used as received. CuBr (99%), 2,7-dibromo-9,9-dihexylfluorene, 4-bromobenzyl alcohol, 2-bromoisobutyryl bromide, tetrakis(triphenylphosphine)palladium(0), *N*,*N*-dimethylacetamide, anisole, and sodium carbonate were purchased from Aldrich Chemical Co. and used without purification.

#### Synthesis of poly[2,7-(9,9-dihexylfluorene)]-*b*-poly[2-(dimethylamino)ethyl methacrylate] diblock copolymers

The synthetic scheme for PF-*b*-PDMAEMA block copolymer is shown in Scheme 1.  $\alpha$ -(4-Hydroxymethylphenyl)- $\omega$ -bromo-

poly[2,7-(9,9-dihexylfluorene)] (3) was synthesized by the Suzuki coupling reaction with 4-bromobenzyl alcohol as the endcapper.9g 2-Bromoisobutyryl bromide (2.0 mL, 16.2 mmol) was added dropwise into a solution of 3 (805 mg, 0.32 mmol) and triethylamine (5.4 mL, 38.4 mmol) in 20 mL dry THF. The mixture was further stirred at room temperature for 24 h and re-precipitated into 200 mL methanol. The collected solid was re-dissolved in 5 mL of THF and re-precipitated twice into 200 mL of methanol to obtain 725 mg of α-{4-[2-(2-bromo-2-methylpropoyloxy)methyl]phenyl}-ω-bromo-poly[2,7-(9,9dihexylfluorene)] (PF-Br) (4) with an  $M_n$  of 2660 (GPC, degree of polymerization = 7) and polydispersity index (PDI) of  $1.26.^{9c}$ PF-b-PDMAEMA copolymers with different coil lengths were synthesized from PF-Br via atom transfer radical polymerization. The preparation of PF7-b-PDMAEMA45 is exemplified below: a dry round-bottomed flask with a magnetic stirrer bar was charged with a mixture of CuBr (14 mg, 0.1 mmol), PF-Br macroinitiator (258 mg, 0.1 mmol), DMAEMA (5.1 mL, 30 mmol), PMDETA (21 µL, 0.1 mmol) and anisole (5 mL). The mixture was degassed and back-filled with nitrogen three times, stirred at ambient temperature for 1 h, and immersed into an oil bath at 110 °C for 5 h. After cooling to ambient temperature, the mixture was passed through an Al<sub>2</sub>O<sub>3</sub> column to remove the copper catalyst and dried under vacuum at 40 °C to obtain PF7-b-PDMAEMA45 (1.25 g) as a brown solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm): 0.88–1.04 (3 H, -CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.81-1.93 (2 H, -CH<sub>2</sub>C(CH<sub>3</sub>)-), 2.27 (6 H, -N(CH<sub>3</sub>)<sub>2</sub>), 2.55 (2 H, -OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 4.04 (2 H, -OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 7.26-7.81 (10 H, fluorene aromatic protons and phenyl end group).

#### Preparation of PF-b-PDMAEMA micelles in solution

The preparation of PF-*b*-PDMAEMA micelles by changing the solvent composition is exemplified below. The aggregates of PF-*b*-PDMAEMA were prepared by first dissolving the copolymer in THF and slowly adding water to the solution to achieve water–THF compositions of 10, 30, 50, 70 and 90 wt%, respectively. Note that the polymer concentration was maintained at 0.1 wt% in the solution. For the thermo-responsive study, PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> in water (0.1 wt%) was raised to 35, 45, 55, 65 or 75 °C, respectively, and held for 48 h to reach thermodynamic equilibrium. For the pH-responsive study, PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub>



Scheme 1 Synthesis of PF-b-PDMAEMA rod-coil diblock copolymers.

aggregates were prepared by dissolution in water and adjusting the pH by either aqueous NaOH or HCl. The final concentration of each sample was set to 0.1 wt% and the solutions were allowed to stand for 48 h for equilibration prior to measurement.

## Characterization

<sup>1</sup>H NMR data was obtained by a Bruker AV 300 MHz spectrometer. Gel permeation chromatographic analysis was performed on a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD GmbH. All GPC analyses were performed on the polymer/THF solution at a flow rate of 1 mL min<sup>-1</sup> at 40 °C and calibrated with polystyrene.

The phase transition of the prepared polymer solution was recorded by monitoring the transmittance of a 550 nm light beam on a Mini 1240 UV-Visible spectrophotometer (Shimadzu). The polymer concentration in water was 0.1 wt%, and the temperature was raised from 25 to 75 °C in increments of 2 °C every 90 min. The micellar aggregates at ambient temperature were characterized by the tapping mode of a MultiMode AFM with a Nanoscope 3D controller (Digital Instruments). For the AFM surface structure at elevated temperature, the MultiMode heater/ cooler was added to provide control of sample temperature. The cantilever used was fabricated from phosphorus-doped Si with a spring constant of 3 N m<sup>-1</sup> and a resonance frequency of 79 kHz. Samples for the AFM measurements were prepared by drop-coating the copolymer solution onto a mica substrate. The specimens were conditioned under air for 24 h to obtain dried samples for characterization. The hydrodynamic diameters of micellar aggregates in water (0.05 wt%) at different temperature was determined by dynamic light scattering (DLS) using a Brookhaven Instruments Zeta Plus apparatus fitted with a 15 mW laser ( $\lambda = 678$  nm) and with the detector set at 90°. Each reported value is the average of 10 measurements.

UV-visible absorption and PL spectra of the copolymer solutions were recorded by a UV-visible spectrophotometer (Jasco V-570) and a Fluorolog-3 spectrofluorometer (Jobin Yvon), respectively. The PL quantum efficiency of PF-*b*-PDMAEMA solution was measured using a Fluorolog-3 with 380 nm excitation, as described in our previous study.<sup>9c</sup>

#### **Results and discussion**

#### Synthesis and characterization

The <sup>1</sup>H NMR spectrum of PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> in CDCl<sub>3</sub> is shown in Fig. S1a<sup>†</sup>. The proton resonances at 0.88–1.04, 1.81–1.93, 2.27, 2.55, and 4.04 ppm are assigned to the methyl, methylene, dimethylamino, methylene (adjacent to the primary amino group), and oxymethylene of the PDMAEMA segment, respectively. The weak signals between 7.26–7.81 ppm are attributed to the fluorene aromatic protons and phenyl end group. The above assignment is compared to the <sup>1</sup>H NMR signals of the PF-Br macroinitiator, as shown in Fig. S1b. Note that PDMAEMA has a much longer chain length than PF, and thus weak signals from the fluorene proton resonances are observed.

The  $M_n$  values of the four PF-*b*-PDMAEMA copolymers were 4900, 7100, 14600, and 29 100 with corresponding PDI values of 1.29, 1.31, 1.36, and 1.39, as shown in Table S1. The estimated

DMAEMA repeating units of four copolymers from  $M_n$  were 31, 45, 93, and 185, and these copolymers are named PF<sub>7</sub>-*b*-PDMAEMA<sub>31</sub>, PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub>, PF<sub>7</sub>-*b*-PDMAEMA<sub>93</sub>, and PF<sub>7</sub>-*b*-PDMAEMA<sub>185</sub>, respectively. Chloroform, THF and toluene are common solvents for both blocks of copolymers, whereas water and methanol are poor solvents for the PF block. The thermal decomposition temperatures ( $T_d$ ) of the copolymers are between 230 and 242 °C (Table S1), which are similar to the PDMAEMA homopolymer ( $T_d = 228$  °C).<sup>14</sup> The DSC thermograms of the copolymers show that the glass transition temperatures ( $T_g$ ) are between 26 and 32 °C, higher than the PDMAEMA homopolymer ( $T_g = 10$  °C)<sup>15</sup> due to the introduction of the rigid PF segment.

# Effect of selective solvent on the surface structures of PF-b-PDMAEMA

Fig. 1 shows AFM images of the structures of  $PF_7$ -*b*-PDMAEMA<sub>45</sub> aggregates with compositions of 0–90 wt% water in THF. Note that the polymer concentration was fixed at 0.1 wt%. Spherical micelles are observed for pure THF and 10 wt% water-THF (Fig. 1a and b), but change to separate cylinders at 30 wt% water-THF (Fig. 1c). Although cylindrical micelles are still observed at 50 wt% water-THF (Fig. 1d), they become shorter.



**Fig. 1** AFM micrographs of  $PF_{7}$ -*b*-PDMAEMA<sub>45</sub> aggregates in water– THF solution with (a) 0, (b) 10, (c) 30, (d) 50, (e) 70 and (f) 90 wt% water.

Structural transformation to exclusively bundles of cylindrical (Fig. 1e) and spiral-shaped (Fig. 1f) micelles are observed at 70 and 90 wt% water–THF, respectively. For the longer coil length copolymer (PF<sub>7</sub>-*b*-PDMAEMA<sub>93</sub>), cylinders and bundles of cylinders are observed at 50 and 90 wt% water–THF, respectively (Fig. 2a and b). Note that spheres, cylinders, and bundles of cylinders for PF<sub>7</sub>-*b*-PDMAEMA<sub>93</sub> are observed at 0, 10, 30, and 70 wt% water–THF (Fig. S4). As the coil length was increased further to PF<sub>7</sub>-*b*-PDMAEMA<sub>185</sub>, the surface structures of bundles of cylinder and spheres are observed at 50 and 90 wt% water–THF, respectively (Fig. 2c and d). Note that the surface structures of spheres, cylinders, and bundles are shown at the water compositions of 0, 10, 30, and 70 wt% water–THF, respectively (Fig. S5).

The above variation of the surface structure with the solvent composition is explained below. Since THF is common solvent for both blocks and water is only a good solvent for PDMAEMA, the PF block domain probably aggregates between solvated PDMAEMA chains with an increasing water content. Also, the mixture of THF and water is microscopically immiscible and may also affect the self-assembly of polymer.<sup>16</sup> At the low water content of 10 wt%, a sphere structure of PF7-b-PDMAEMA<sub>45</sub> is observed, but changes to cylindrical aggregate as the water content is increased to 30 and 50 wt%. Such structural transformation is probably explained by the driving force of  $\pi$ - $\pi$  interaction among fluorene segments down the long axes of the cylinders.1a The cylindrical micelle has a height and width of about 84 and 82 nm (Fig. 3a), respectively. Further enhancing the water content to 70 wt%, bundles of cylinders are formed with height and width of about 160 and 352 nm (Fig. 3b), suggesting further aggregation has arisen to minimize the interfacial energy between the PF and water as the water content is increased. Finally, a spiral-shaped structure with several loops appears at 90 wt% water. The cylindrical bundles are observed at



Fig. 2 AFM micrographs of PF-*b*-PDMAEMA aggregates in water– THF solution with (a) 50 wt%; (b) 90wt% water for PF<sub>7</sub>-*b*-PDMAEMA<sub>93</sub>, and (c) 50 and (d) 90 wt% water for PF<sub>7</sub>-*b*-PDMAEMA<sub>185</sub>, respectively.



Fig. 3 Two-dimensional AFM micrographs (upper) and the corresponding cross-sectional surface images (lower) of  $PF_{7}$ -b-PDMAEMA<sub>45</sub> aggregates in water–THF solution with (a) 50 and (b) 70 wt% water, respectively.

a lower water content (50 wt%) for the longest coil length of PF7b-PDMAEMA<sub>185</sub>, compared to those of the other two copolymers. Since the hydrophilic characteristic of the copolymers would be stronger for a longer PDMAEMA, formation of cylindrical bundles of the hydrophobic PF is promoted. The unusual spiral-shaped structure is not observed at the longer coil length for the other two copolymers. Instead, cylindrical bundles and spherical structures are observed at 90 wt% water for PF7-b-PDMAEMA<sub>93</sub> and PF<sub>7</sub>-b-PDMAEMA<sub>185</sub>, respectively. As reported in the literature, the spiral-shaped structure is related to the length of coil block, the solution composition, the substratesolution interfacial tension, and the long-range electric dipolar interaction.<sup>17</sup> Rod-coil block copolymers with a high coil fraction lead to a large chain mobility, disordering the rigid rod block.<sup>7a-c</sup> Therefore, it would be difficult to form a long-range-ordered arrangement of spiral-shaped or bundle structures from PF7-b-PDMAEMA<sub>185</sub>, with a long coil length, thus explaining the above difference in surface structures at 90 wt% water-THF.

# Effect of temperature on the surface structures of PF-*b*-PDMAEMA

PDMAEMA has an LCST of 32–52 °C,<sup>12a</sup> depending on its molecular weight. Fig. 4 shows the transmittance (at 550 nm) vs.



**Fig. 4** Variation of optical transmittance with temperature (25–75 °C): (a) PF<sub>7</sub>-*b*-PDMAEMA<sub>31</sub> ( $-\bullet$ -), (b) PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> ( $-\bullet$ -), (c) PF<sub>7</sub>-*b*-PDMAEMA<sub>93</sub> ( $-\bullet$ -), (d) PF<sub>7</sub>-*b*-PDMAEMA<sub>185</sub> ( $-\bullet$ -).

temperature curves of the four studied copolymers, in which all the PF-*b*-PDMAEMA copolymers exhibit an LCST around 40 °C. Note that the optical absorption edge of the PF segment is around 440 nm and thus would affect the observation of LCST by optical transmission at 550 nm. This suggests that the short PF segment is not enough to change the LCST character of PDMAEMA. However, the copolymer with a longer PDMAEMA chain length has a sharp transition, since such a copolymer would approach similarity to the PDMAEMA homopolymer.

Fig. 5 shows the variation in the surface structures of PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> in water with temperature. The surface structure is cylinder-bundles at 25 °C (below the LCST) (Fig. 5a, average diameter of bundles = 430 nm), but changes to cylinders at 45 °C

(above the LCST) (Fig. 5b, average cylindrical diameter = 80 nm), spheres at 55 °C (Fig. 5c, average spherical diameter = 110 nm) and aggregate spheres at 75 °C (Fig. 5d, average spherical diameter = 480 nm). Structural transformation of micelles with temperature also occurs at longer PDMAEMA coil lengths,  $PF_{7}$ -b-PDMAEMA<sub>185</sub> (Fig. S6). Below the LCST, the coronas of spherical micelles are in a swollen state. When the temperature is increased progressively to 55 and 75 °C, there are aggregations of spherical micelles.

The above structural change on the micelle can be attributed to the variation in the hydrophilic/hydrophobic property of PDMAEMA. The thermoresponsive PDMAEMA block is highly hydrated and adopts an extended corona conformation below its LCST. However, as the temperature is raised above the LCST, the intramolecular hydrogen bonding between the C=O groups of the PDMAEMA chains results in a compact and collapsed conformation, thus excluding water molecules from the corona. Therefore, the radii of cylindrical micelles become smaller (Fig. 5b). Further increasing the temperature to 55-75 °C enhances the intramolecular hydrogen bonding of the corona, and thus the corona becomes highly contracted, disrupting the PF aggregation. Thus, spherical micelles of PF7-b-PDMAEMA45 are observed (Fig. 5c and 5d). Aggregate spherical micelles of PF7-b-PDMAEMA<sub>185</sub> are observed at higher temperatures (55-75 °C, above the LCST), because the long hydrophobic PDMAEMA segment reduces the colloidal stability in water, resulting in interconnected larger micelles (Fig. S6).

The thermoresponsive behavior of the copolymers was also monitored by variable-temperature DLS measurements. Fig. 6a shows the DLS results for aqueous solutions of  $PF_{7}$ -*b*-PDMAEMA<sub>45</sub> at different temperatures. When the solution was



**Fig. 5** AFM micrographs of  $PF_{7-}b$ -PDMAEMA<sub>45</sub> aggregates in water by increasing temperature at (a) 25, (b) 45, (c) 55 and (d) 75 °C, respectively.



Fig. 6 Hydrodynamic diameter of (a)  $PF_{7}$ -b-PDMAEMA<sub>45</sub> and (b)  $PF_{7}$ -b-PDMAEMA<sub>185</sub> aggregates in water with changing temperature.



Fig. 7 Variation of optical transmittance of  $PF_{7}$ -b-PDMAEMA<sub>45</sub> in water when subjected to a heating-cooling cycle between 25–60 °C.

heated from 25 to 45 °C, the hydrodynamic diameter of the polymer micelles in solution decreased from 2200 to 960 nm. Further heating to 55 °C resulted in a drastic decrease in the hydrodynamic diameter to 95 nm. Such variability is consistent with the contraction of PDMAEMA corona induced by the formation of intramolecular hydrogen bonding. But heating the solution to 75 °C caused an increase in hydrodynamic diameter to 460 nm, suggesting the micelles changed into an agglomerated insoluble state. The DLS results for an aqueous solution of PF7b-PDMAEMA<sub>185</sub> are shown in Fig. 6b. This shows clearly that the hydrodynamic diameter increases when the temperature is increased due to further dehydration and aggregation of the PDMAEMA blocks when the temperature is above the LCST. The micelle sizes from DLS measurements are different from those from AFM, since the former used liquid samples, but the latter used dried samples. However, the trend in the variation of the micelle size with temperature is the same.

Fig. 7 shows the optical transmittance of PF7-b-PDMAEMA<sub>45</sub> in water when subjected to a heating and cooling cycle. The surface structures of PF7-b-PDMAEMA45 during the cooling are identical to the heating process (Fig. S7). The reversible optical transmittance and identical structures suggest that the thermoresponsive behavior of PF7-b-PDMAEMA45 is reversible. However, hysteresis on the interchange association between the PDMAEMA blocks and the dissolution of polymer chains in water occurs during the heating and cooling cycle. Previous studies<sup>18</sup> in PNIPAAm clearly revealed that the hysteresis is due to the formation of intra- and interchain hydrogen bonds between different chain segments when they are overlapped in the collapsed state. Such hydrogen bonds cannot be completely removed in the cooling process, even when the temperature is lower than the LCST. The present structure variation on the PF7-b-PDMAEMA45 shows a similar behavior.

#### pH-Responsive behavior of PF7-b-PDMAEMA45

Fig. 8 shows the structural change of the  $PF_{7}$ -*b*-PDMAEMA<sub>45</sub> micelles in water induced by pH variation. As the pH increases from 2 to 7, spherical micelles are observed and the diameter of micelles decreases from 215 to 150 nm. The pH value controls the



Fig. 8 AFM micrographs of  $PF_7$ -b-PDMAEMA<sub>45</sub> aggregates in water at (a) pH 2, (b) pH 7 and (c) pH 10, respectively.

degree of charge in the corona of the PDMAEMA block and induces swelling or shrinking due to the electrostatic repulsion.<sup>12b,12c</sup> The reduction in micellar diameter upon increasing pH is probably due to the suppressant electrostatic repulsion on the charged PDMAEMA chains in the corona. However, the surface structure changes into bundles of cylinders at pH 10 (Fig. 8c), where the PDMAMEA blocks are almost deprotonated and aggregated. Thus, the different polarities of PDMAMEA and PF induce a  $\pi$ - $\pi$  interaction between the PF blocks, which then undergo further association to form cylindrical micelles. The state of protonation or deprotonation of PDMAEMA is a critical parameter for the resultant polymer structure. Similar structural transformations were also observed for the poly( $\varepsilon$ caprolactone)-*b*-PDMAEMA rod-coil copolymer in water by varying the pH.<sup>12b</sup>



Fig. 9 Variation of LCST of PF7-b-PDMAEMA45 with pH value.

The effect of pH on the LCST is shown in Fig. 9. As the pH of the polymer solution increases, a reduced LCST is observed. The strong electrostatic repulsion existing between protonated PDMAEMA blocks at acidic pH results in a well-swollen corona as the temperature is increased. In contrast, deprotonation occurs on PDMAEMA at basic pH, promoting intramolecular hydrogen bonding and leading to a low LCST. However, no LCST is observed at pH 2, suggesting that the strong electrostatic repulsive force keeps the PDMAEMA blocks well-extended below the boiling point of water.

# Variation in photophysical properties of PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> with varying temperature and pH

Fig. 10 shows the optical absorption and PL spectra of 0.1 wt% PF7-b-PDMAEMA45 in 0 to 100 wt% water-THF. As shown in Fig. 10, the absorption peak maximum shifts from 376 to 367 nm as the water content increases, which is a result of the  $\pi$ - $\pi$ transition of the PF block. Such a blue shift suggests the reduction of the effective conjugated lengths of the PF is due to the less planar backbone resulting from its poor solvation in water. A strong fluorescence quenching, with the quantum efficiency reduced from 0.82 to 0.15, was also observed as the water content was increased. In addition, an apparently broadened shoulder at around 440 nm is shown in the PL spectra. This indicates that intermolecular aggregations of PF-b-PDMAEMA chains could lead to fluorescence quenching and a hypsochromic (blue) shift in the absorption spectra. These phenomena are probably explained by assuming H-type aggregation formed by a parallel orientation of PF segments<sup>19</sup> similar to those reported for other rod-coil block copolymers7d,e and in other studies by ourselves.9c

Fig. 11 shows the PL spectra of 0.1 wt% PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> in water when subjected to a heating and cooling cycle between 25 and 75 °C. The PL intensity reduces upon increasing temperature and increases again with reducing temperature. This thermoresponsive behavior can be explained by the appearance of the intramolecular hydrogen bonding of PDMAEMA chains. Heating the copolymer solution above the LCST induces a densely packed PDMAEMA corona and suppresses the ability of the PF core to absorb the incident light. However, cooling the



Fig. 11 Photoluminescence spectra of  $PF_{7}$ -*b*-PDMAEMA<sub>45</sub> aqueous solution in the temperature range of 25–75 °C: (a) heating; (b) cooling.

solution below the LCST leads to a swelling of the PDMAEMA corona in water, allowing incident light absorption by the PF core and resulting in a relatively strong emission intensity. Such structural change of micelle leads to the reversible expression of "on–off" fluorescence intensity profile shown in Fig. 11.

Fig. 12 shows a three-dimensional plot of the variation of PL intensity of 0.1 wt% PF<sub>7</sub>-b-PDMAEMA<sub>45</sub> in water with temperature and pH. At 25 °C, the PL intensity is weak at acidic pH, but becomes strong as the pH is increased, showing a typical "off–on" fluorescence intensity profile. The protonation of the PDMAEMA chains at acidic pH leads to the formation of large polymer spheres and scarcely any absorbance of the incident light of the PF core, resulting in weak emission intensity. In contrast, the cylinder copolymer at basic pH enhances the absorption of incident light by the PF core, leading to a strong emission intensity. At the temperature is increased to 55 °C, the PL intensity at acidic and basic pH are both weak, but is relatively strong at neutral pH, showing an "off–on–off" profile. The



Fig. 10 Optical absorption and photoluminescence spectra of  $PF_7$ -b-PDMAEMA<sub>45</sub> in 0 to 100 wt% water-THF solution.



**Fig. 12** Three-dimensional plot of the variation of photoluminescence intensity of PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> with temperature and pH.

PL intensity turns into an "on–off" profile at 75 °C. Such a switch in the PL intensity profile is due to the temperatureinduced phase transition of the copolymer. The LCST of the PF<sub>7</sub>-*b*-PDMAEMA<sub>45</sub> is strongly dependent on the solution pH: it decreases with increasing pH, as discussed above. Therefore, the copolymer at a basic pH quickly precipitates as a higher temperature and leads to a lower PL intensity. At an acidic pH, the polymer micelles remain soluble and show an unchanged emission intensity as the temperature is raised. The on–off characteristic of PL intensity indicates that the prepared copolymers actually behave as a configurable fluorescent indicator of the pH window driven by temperature.

# Conclusion

We have successfully prepared new PF-b-PDMAEMA rod-coil block copolymers showing a significant variation in their surface structure and photophysical properties with respect to solvent composition (water-THF), temperature, and pH. The surface structures of PF7-b-PDMAEMA45 varied from spheres, to separate cylinders, to bundles of cylinders and finally spiralshaped micelles as the solvent composition changed from 0 to 90 wt% water-THF. However, the long-range order structure of spiral-shaped loops was not observed at a long coil length. The micellar aggregate of PF7-b-PDMAEMA45 in water showed a reversible change of surface structure from cylinder-bundles to spheres over a heating-cooling cycle of 25-75 °C. The LCST of the PF7-b-PDMAEMA45 decreases with increasing pH, depending on the protonation to the PDMAEMA block. The PL intensity of PF7-b-PDMAEMA45 in water was thermoreversible based on its LCST. The PL characteristics suggested that the new copolymers behaved as on/off fluorescence indicator of temperature or pH, with a reversible "on-off" profile at an elevated temperature in water: the pH-fluorescence intensity switched from "off-on" to "on-off" profiles as the temperature increased. This study suggests that the PF-b-PDMAEMA copolymer has potential applications as a multifunctional sensory material toward solvent, temperature, and pH.

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