

Copolymer logical switches adjusted through core–shell micelles: from temperature response to fluorescence response†

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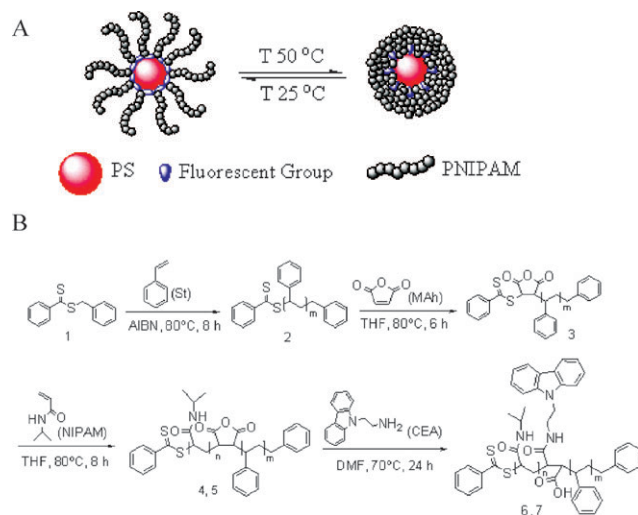
Aqueous solution of micelles prepared from novel PS-*b*-PNIPAM with fluorescent group CEA at the junction between two blocks displays logical responsive switches on temperature and fluorescence; at lower temperature, stretching of PNIPAM chains causes high mobility of CEA leading to formation of more excimer species; at higher temperature, shrinking of PNIPAM chains isolates the fluorescent groups between the core and shell, resulting in fewer excimer species.

Formation and photoluminescence of core–shell aggregates from self-assembly amphiphilic block copolymers containing chromophores have attracted great attention due to their engrossing properties and potential applications.¹ For example, fluorescent chemosensors allow a rapid detection of analyte in solution by simple emission enhancement or quenching.² Recently, fluorescent temperature sensors, in which the emission intensity is controlled by temperature of solution, have been extensively studied.³ However, the control of fluorescent intensity by temperature of aqueous solution based on copolymers is less researched, and the principle reported is almost the same based on dependence of polarity in the polymer domains with temperature.⁴ Shiraishi *et al.* reported the synthesis of poly(NIPAM-*co*-HC), a polymer consisting of *N*-isopropylacrylamide (NIPAM) and hemicyanine dye (HC)-substituted methylstyrene units. With weak fluorescence in polar media and strong fluorescence in less polar media, the chromophores (HC) exhibit great sensitivity to the polarity of the environment. Poly(NIPAM-*co*-HC) has high polarity at low temperature (coil), and less polar domains inside the polymer aggregates leads to strong fluorescence at high temperature.⁵ Therefore, finding a new principle of the polymer chemosensors is significant for creating of new polymer-based fluorescent thermometers.

Fluorescent properties of poly(*N*-vinylcarbazole) (PVCz) has been well studied and two fluorescence emissions appear at ~370 and ~420 nm, which correspond to two excimer species arising from partially and totally face-to-face overlapped carbazole groups, respectively.⁶ For the random poly(VCz-*co*-St) with different compositions of VCz and styrene (St), the emission

intensity monotonically decreases as the carbazole (Cz) content decreases. When the VCz unit content is below 15 mol%, the emission intensity is very weak because VCz units are quite separated due to less content of VCz–VCz sequences in the polymer chains, and the excimer species formation are relatively low.⁷ Based on these evidences, we have designed a system which emits strong fluorescence at low temperature, but weak fluorescence at high temperature. The mechanism is that at low temperature, the concentration of Cz groups in a local area is high, leading to the formation of more excimer species. At high temperature, the Cz groups are isolated by polymer chains, resulting in fewer excimer species. Such a system is a micelle with polystyrene (PS) as the core and PNIPAM as the shell with Cz groups located in the middle layer between the core and the shell. PNIPAM is a well-known temperature sensitive polymer whose critical solution temperature (LCST) is around 32 °C;⁸ below 32 °C the polymer shows strong fluorescence because the PNIPAM chains are stretched out and more excimer species are formed, but above 32 °C, PNIPAM chains shrink and Cz groups are isolated by polymer chains, resulting in weak fluorescence (Scheme 1A). Since the PNIPAM in water shows a reversible coil-to-globule phase transition,⁹ the polymeric fluorescent thermometers could be recycled.

To test the aforementioned idea, we first synthesized a novel amphiphilic block copolymer PS-*b*-PNIPAM with *N*-carbazole ethylamine (CEA) at the junction between the two blocks (PS-(MAh-*g*-CEA)-*b*-PNIPAM). Although the polymers



Scheme 1 (A) Schematic representation of effect of temperature on the distribution of fluorescent groups in the micelles; (B) synthetic route toward the novel fluorescent amphiphilic copolymer *via* the RAFT process.

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end-capped with the fluorescent group have been studied, to the best of our knowledge, the synthesis of block copolymers with fluorescent groups at the junction between two blocks has not been reported.¹⁰ We synthesized PS-(MAh-g-CEA)-*b*-PNIPAM according to Scheme 1B, with the PS block synthesized by reversible addition–fragmentation transfer (RAFT) polymerization of St in the presence of chain transfer agent (CTA, **1**) and 2,2-azobis(isobutyronitrile) (AIBN). The PS **2** with $M_{n, GPC} = 3550$, $M_w/M_n = 1.14$ was obtained, and then a single maleic anhydride (MAh) was introduced to form macro RAFT agent **3**, which was verified by the methine proton signal in the MAh unit at δ ca. 4.34–4.38 ppm (Fig. S1b in ESI†).¹¹ It was used in further RAFT polymerization of NIPAM with the molar ratio of [AIBN]:[macro-CTA]:[NIPAM] = 0.2:1:200 (Table S1, ESI†), and PS-MAh-*b*-PNIPAM **4**, **5** ($M_{n, GPC} = 8400$ and 12900, $M_w/M_n = 1.29$ and 1.31, respectively) were produced. The molecular weights were controlled by feed molar ratio and conversion (Fig. S1, ESI†), and the structures were confirmed by ¹H NMR spectra (Fig. S2, ESI†), with the characteristic proton signals of phenyl groups in PS at δ 6.3–6.8 and 6.85–7.25 ppm, and the methine proton signal of the isopropyl group in PNIPAM at δ 3.98 ppm. After MAh in the copolymer chains reacted with the fluorescent compound CEA (Table S2 in ESI†), the block copolymers **6** and **7** were prepared (detailed synthetic procedures in ESI†). The signals at δ 8.08 and 7.46 ppm ascribed to carbazole group indicates that the synthesis was successful. For preparation of micelles by self-assembly, the amphiphilic copolymer PS-(MAh-g-CEA)-*b*-PNIPAM **6** or **7** was dissolved in DMF to form a solution with concentration of 2.0 mg mL⁻¹, and the deionized water was dropped into this solution at a rate of 0.2 mL min⁻¹ at room temperature by a microsyringe. A micellar solution with concentration of 0.44 mg mL⁻¹ (DMF:H₂O = 3.5:1, v/v) was obtained.

Similar to the investigation of temperature responsive switch reported,¹² we utilized laser light scattering (LLS) to study the temperature dependence of the polymeric core–shell micelles in aqueous solution. We can see in Fig. 1A that with the increase of temperature from 24 to 50 °C, the hydrodynamic diameter (D_h) decrease of the micelles started from 32 °C, indicating that water became a poor solvent for PNIPAM blocks. Then the stretching PNIPAM chains shrunk and collapsed on the surface of the PS core, leading to the decrease of D_h from 87.7 to 55.8 nm for PS₃₂-(MAh-g-CEA)-*b*-PNIPAM₈₁ (copolymer **7**), and 66.4 to

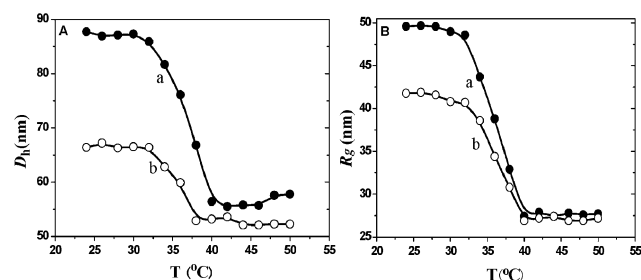


Fig. 1 (A) Hydrodynamic diameter vs. temperature of copolymer **7** (a) and **6** (b). (B) Temperature dependence of R_g of copolymer **7** (a) and **6** (b). The concentrations of all samples in aqueous solution were 0.44 mg mL⁻¹.

52.2 nm for PS₃₂-(MAh-g-CEA)-*b*-PNIPAM₄₁ (copolymer **6**). The critical transition temperatures of the copolymers **6** and **7** are 34.5 and 35.7 °C, respectively. The relationship of statistic radius (R_g) with temperature in Fig. 1B shows the great size variation of the core–shell micelles with the rise of temperature. The R_g decreased sharply from 49.6 to 27.8 nm for copolymer **7** and from 41.8 nm to 26.9 nm for copolymer **6**. Moreover, the hydrodynamic diameter distributions, $f(D_h)$ of the copolymers **6** and **7** with different PNIPAM chain lengths are very narrow, and the maximum values of the hydrodynamic diameter are around 75 and 94 nm, respectively, according to the results of dynamic light scattering (DLS). All the facts indicate that the amphiphilic block copolymer chains were self-assembled into core–shell micelles, and the aqueous micellar solution displayed a phase transition induced by temperature variation. This reflects that the PNIPAM chains stretched out at <30 °C, and collapsed on the surface of the PS cores at >40 °C.

In order to investigate the effect of structural variation of the micelles on their fluorescence property, solutions of copolymers **6** and **7** were prepared in DMF–H₂O (3.5:1, v/v) with a micelle concentration of 0.44 mg mL⁻¹, their UV-vis spectra were measured at 25 and 45 °C, respectively and are shown in Fig. 2A. By comparison, UV-Vis spectrum of CEA is also

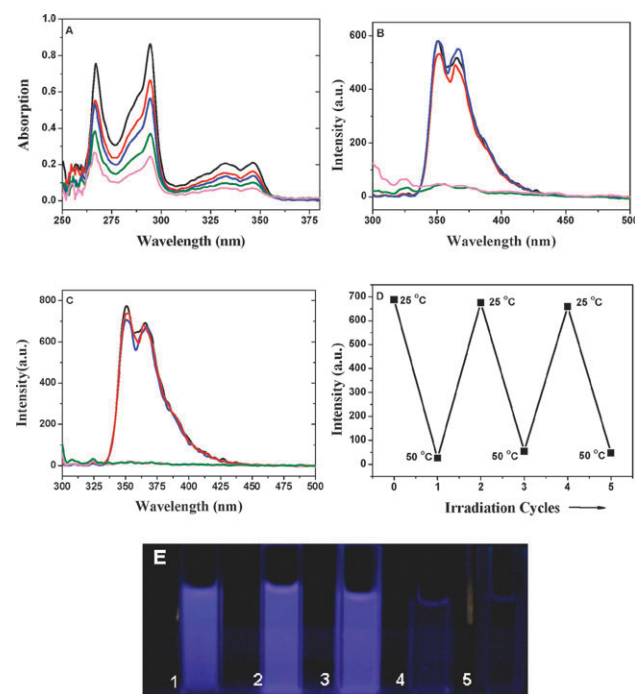


Fig. 2 (A) UV-Vis spectra of CEA (black, at 25 °C), copolymer **6** (red, at 25 °C), copolymer **7** (blue, at 25 °C), copolymer **6** (green, at 45 °C), copolymer **7** (pink, at 45 °C). (B) Fluorescence spectra of CEA (black, at 25 °C), copolymer **6** (red, at 25 °C), copolymer **7** (blue, at 25 °C), copolymer **6** (green, at 45 °C), copolymer **7** (pink, at 45 °C); $\lambda_{ex} = 266$ nm. (C) Fluorescence spectra of above samples, $\lambda_{ex} = 295$ nm. (D) Fluorescent cycling of copolymer **6** at various temperatures between 25 and 50 °C; $\lambda_{ex} = 295$ nm. (E) Photographs of solutions containing (1) CEA (25 °C), (2) copolymer **6** (25 °C), (3) copolymer **7** (25 °C), (4) copolymer **6** (45 °C), (5) copolymer **7** (45 °C), taken when the samples were exposed to UV-light irradiation, 254 nm, at different temperature. (The concentration of the fluorescent group in all solutions was 5×10^{-5} mol L⁻¹, DMF/H₂O = 3.5/1, v/v)

shown in Fig. 2A. All spectra demonstrate almost the same absorption bands at around 266, 295, 332 and 346 nm. Comparing the UV-vis spectra measured at 25 °C with those at 45 °C, we find that absorption intensity of the copolymers measured at 45 °C decreased sharply because the solubility of PNIPAM becomes worse in water. The aggregation of micelles occurs, which leads to reduction of light transmittance. When UV at $\lambda = 266$ or 295 nm was used to excite the fluorescence of aqueous solution of free CEA, and aqueous solution of micelles containing CEA group at 25 °C, two strong fluorescence emissions appeared at 353 and 368 nm (Fig. 2B and C). When the solution temperature was raised to 45 °C micellar fluorescent quenching was found to occur in copolymers **6** and **7**. However, when the temperature was returned to 25 °C, the fluorescence became its original value (Fig. 2B and C). To observe directly the fluorescence variation of micellar solution with temperature, UV at 254 nm was used to excite the solutions of CEA and copolymers **6** and **7**; a blue color could be observed for the solutions of CEA, copolymers **6** and **7** measured at 25 °C, but emission of polymer solution was quenched almost completely at 45 °C (Fig. 2E). These results confirm that the block copolymers can act as logical responsive switches on temperature and fluorescence through temperature variation. Probably, water is a good solvent for the PNIPAM, so all PNIPAM chains in the shell of the micelles are stretched out at 25 °C and the fluorescent groups at the junction of the two blocks have high mobility, thus the Cz–Cz excimers are readily formed and their high concentration in the middle layer of the micelles may be another reason. At 45 °C, which is higher than LCST of the copolymer, the water becomes a worse solvent for PNIPAM, and the polymer chains shrink and collapse onto the surface. The fluorescent groups are isolated by polymer chains, and the formation of excimer species becomes difficult, resulting in the fluorescence quenching. The architectural change leads to micellar fluorescent switch property, as explored between 25 and 50 °C. The results shown in Fig. 2D demonstrate that there was 22 times fluorescent enhancement when temperature of the solution decreased from 50 to 25 °C, which is higher than previous data reported.⁵ The PNIPAM chains display a well reversible coil-to-globule phase transition, and the fluorescent property of the block copolymer is completely reversible (Fig. 2D). The good temperature-dependent fluorescent properties should be ascribed to the structure of block copolymer, and in turn, to the structure of their micelles; block copolymers with a single fluorescent group at the middle of the chain is different from with the fluorescent group at the chain end.¹⁰ Self-assembly of the latter forms micelles with fluorescent groups in the core, and fluorescence intensity of the polymer solution has little dependence on temperature.

In conclusion, the block copolymers, PS-(MAH-*g*-CEA)-*b*-PNIPAM have been successfully prepared, and their self-assembly in aqueous solution produces micelles with fluorescent group CEA in the middle layer between the shell and

core. The micelle solution displays strong fluorescence at 25 °C, but very weak emission at 45 °C. The principle for logical responsive switches on temperature and fluorescence relies on the formation of more excimer species due to high mobility and high concentration of CEA groups at low temperature, and fewer excimer species formed due to the isolation of the CEA groups by polymer chains at high temperature. The block copolymers might have potential application in biosensors, molecular probes and smart polymer machines.¹³

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