Polymeric Temperature and pH Fluorescent Sensor Synthesized by Reversible Addition–Fragmentation Chain Transfer Polymerization

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ABSTRACT: Simple-structured copolymer, poly(NIPMAM-*co*-CPMA), consisting of *N*-isopropylmethacrylamide (NIPMAM) and (*Z*)-4-(1-cyano-2-(4-(dimethylamino) phenyl)vinyl)phenylmethylacrylate (CPMA) units as thermo- and pH-responsive fluorescent signaling parts, respectively, has been synthesized by reversible addition–fragmentation chain transfer polymerization. The copolymer PCN250 ($m/n = 250$) shows absorbance enhancement or decrease at different pH value. However, the fluorescence intensity of this copolymer shows enhancement with a rise in temperature regardless of pH value in the range of pH = 4–10. In addition, fluorescence suppression of copolymer (PCN250) was observed with high proton concentration. Moreover, the lower critical solution temperature of the copolymers, poly-(NIPMAM-*co*-CPMA), with different component was also investigated. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2219–2226, 2012

KEYWORDS: living radical polymerization (LRP); *N*-isopropylmethacrylamide; pH; reversible addition–fragmentation chain transfer polymerization; sensors; stimuli-sensitive polymers; temperature

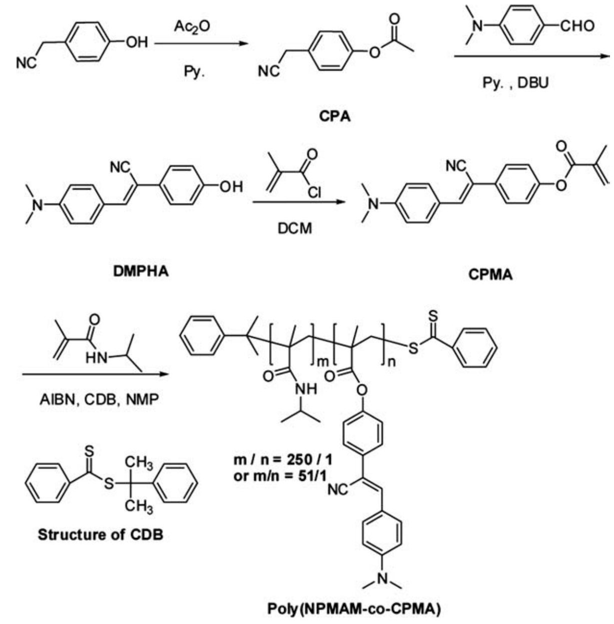
INTRODUCTION Among manifold stimuli-responsive polymeric materials, polymeric pH sensors have received increasing attention in recent years.[1–7] pH is an important factor that is closely related to physiological activity, so quantitatively measuring pH is useful for cellular analysis or diagnosis. However, most proton sensors are limited to the narrow pH response, ranging mainly 3–12.[2,3,7] Sensors with high proton concentrations are rarely studied,[4] which restrict the further application in some special fields, such as water pollution evaluation, sewage treatment, and so on.

Other stimuli-responsive polymeric materials, such as polymeric thermometers, also have attracted increasing research interest.[8–21] These fluorescent thermometers allow "remote" sensing of medium temperature, where no electric wires are required to connect the thermometers. These thermometers therefore have advantages over traditional thermometers in applications where electromagnetic noise is strong, sparks could be hazardous, and the environment is corrosive. Poly(*N*-isopropylmethacrylamide) (PNIPMAM) materials have been considered as a well-known member of molecular thermometers in several years.[14,22,23] Around a specified temperature, commonly referred to as a lower critical solution temperature (LCST), PNIPMAM in aqueous solutions undergo a coil-to-globule phase transition due to the destruction of intermolecular hydrogen bonding between polymer chains and water.

A current trend of optical sensor is the development of dual sensors that respond simultaneously and independently to different stimuli, such as pressure and temperature,[24] oxygen and temperature,[25,26] oxygen and carbon dioxide,[27,28] oxygen and pH value[29,30] as well as temperature and pH value.[13,31] We aimed to prepare a dual fluorescent sensor that respond to both pH and temperature, which would be beneficial, for example to monitor chemical reactions and for biological diagnostics.

As the solubility transition of the polymer is dependent on the corresponding molar mass distribution, a well-defined polymer is required. While most of the previous polymer sensors were synthesized by ordinary radical polymerization, which was difficult to control the molecular weight, polydispersity, and molecular topology, and consequently negatively affected the sensing capacity.[32] Therefore, a controlled radical polymerization, reversible addition–fragmentation chain transfer (RAFT) polymerization, was applied to prepare the copolymer poly(NIPMAM-*co*-CPMA) (Scheme 1) to avoid or reduce the aforementioned shortcomings. RAFT was one of the most promising controlled/living radical polymerization methods that can control the polymer molecular weight and its distribution with the usage of chain transfer agent,[33,34] such as esters disulfide compounds. This attractive method for the synthesis of fluorescent polymers with desirable polymerization degrees and low polydispersity was first used

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



SCHEME 1 Synthesis of poly(NIPMAM$_m$-*co*-CPMA$_n$) (m/n = 250/1 or m/n = 51/1).

in proton and fluoride sensing in our recent research.[4,35,36] Up-to-date, only few studies that report on controlled copolymers about pH and temperature sensing with chromophores in the PNIPMAM exist.[22]

Herein, smart copolymers of PCN250 and PCN51, prepared by RAFT polymerization, have been designed for pH and temperature sensing based on the hydrophobicity/hydrophilicity balance of copolymer chain. The molecular weights and the monomer content copolymer were well controlled by the RAFT method. The LCST and pH behavior of the resulted copolymers with different pH have been investigated in detail.

EXPERIMENTAL

Materials

All solvents were of analytical grade and used without further purification. NIPMAM was synthesized according to the procedure described previously.[22] NIPMAM monomer was used after recrystallization from *n*-hexane. Water was purified by the MilliQ system. The synthesis route of the copolymers is summarized in Scheme 1.

Methods

All of the spectroscopic measurements were carried out with a 1-cm path length quartz cell. Fluorescence spectra were measured on a HORIBA fluorescence spectrophotometer (λ_{exc} = 380 nm, λ_{em} = 480 nm) equipped with a temperature controller. UV–vis spectra were obtained using a Varian Cary 500 spectrophotometer (1 cm quartz cell). The measurements took place in the temperature range from 15 to 65 °C with a heating/cooling rate of 1 °C/min. The measurements were carried out after the solution was left for 2 min at the designated temperature with magnetic stirring. ^{1}H NMR and ^{13}C NMR in $CDCl_3$ or DMSO-d_6 (dimethylsulfoxid) were measured on a Bruker AV-400 spectrometer with tetramethylsilane as internal standard. Fast-atom-bombardment mass spectrometer (FAB-MS) spectra were obtained by a JEOL JMS 700 mass spectrometer. The pH value was checked by pHS-25 with a range from pH 0 to 14. The number-average molecular weights (M_n) and polydispersity (M_w/M_n) of the copolymers were measured by gel permeation chromatography (GPC) with RI (Infrared spectrometer) detector at 30 °C using THF as eluent and standard polystyrene as the reference (Waters 1515/Wyatt Technology Corp.).

Synthesis of CPA

A stirred mixture of 2-(4-hydroxyphenyl) acetonitrile (13.3 g, 0.1 mol) and acetic anhydride (30 mL) dissolved into pyridine (25 mL) was heated to 120 °C for 4 h, after concentrated in vacuo, cooled and poured into ice water (350 mL) slowly with stirring. Sodium carbonate was added to neutralize the solution and it was extracted twice with ethyl acetate (200 mL). After concentrated in vacuo, petroleum ether (150 mL) was added and a great deal of white solid 4-(cyanomethyl)phenyl acetate (CPA) (17.2 g, 98.5%) was crystallized from the solution. m.p. 42–43 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): δ = 7.35 (d, 2H, H—Ph, J = 8.5 Hz), 7.11 (m, 2H, H—Ph, J = 8.5 Hz), 3.72 (d, 2H, CH_2—CN, J = 20.8 Hz), 2.26 (m, 3H, CH_3—CO).

Synthesis of DMPHA

CPA (4.45 g, 25.4 mmol), 4-dimethylamino benzaldehyde (3.80 g, 25.4 mmol) and 1,8-diazabicyclo (5,4,0) undec-7-ene (DBU) (3.87 g, 25.4 mmol) were dissolved in pyridine (30 mL) and stirred for 18 h at 100 °C under argon, then cooled, poured into deionized water (180 mL). Here, the product had hydrolyzed to be a corresponding phenol. The solution was extracted three times with dichloromethane (150 mL) and the underlayer was washed three times with water (90 mL). After drying with anhydrous $MgSO_4$ and concentrated in vacuo, the residue was applied to silica gel chromatography (petroleum ether:ethyl acetate = 5:1) to afford yellow compound (Z)-3-(4-(dimethylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (DMPHA) (2.69 g, 34.6%). m.p. 214–215 °C.

^{1}H NMR(400 MHz, $CDCl_3$, δ, ppm): δ = 8.72 (d, 2H, H—Ph, J = 9.0 Hz), 7.51 (m, 2H, H—Ph, J = 8.5 Hz), 7.29 (s, 1H, =CH—CN), 6.87 (m, 2H, H—Ph, J = 8.5 Hz), 6.72 (d, 2H, H—Ph, J = 9.0 Hz), 3.05 (s, 6H, CH_3—N). High resolution mass spectrometer (HRMS) (m/z): calcd for $C_{17}H_{16}N_2O$, 264.1263, found, 265.1335 $[M+H]^+$.

Synthesis of (*Z*)-4-(1-Cyano-2-(4-(dimethylamino) phenyl)vinyl)phenylmethylacrylate

DMPHA (0.68 g, 2.59 mmol) was dissolved in dichloromethane (10.0 mL) and triethylamine (0.4 mL, 2.59 mmol) and stirred in ice bath under argon. Then methacryloyl chloride 0.25 mL (2.59 mmol), which was dissolved in dichloromethane (10.0 mL), was dropped for 1 h. After stirring for 16 h at room temperature, the solution was poured into deionized water (100 mL) and extracted with dichloromethane (40.0 mL) four times. After drying with anhydrous $MgSO_4$ and concentrated in vacuo, the crude product was recrystallized two times by ethanol to afford brown compound (Z)-4-(1-cyano-2-(4-(dimethylamino) phenyl)vinyl)phenylmethylacrylate (CPMA; 0.75 g, 86.9%).

TABLE 1 Molecular Weights and Polydispersity Indexes of the Copolymers Prepared by RAFT Polymerization

Polymer	[NIPMAM]/[CPMA]/[CDB]/[AIBN]	$M_{n(Theor.)}$	$M_{n(GPC)}$	PDI (M_w/M_n)	CPMA (%)
PCN51	300/6/2/1	13,000	11,500	1.29	1.9
PCN250	312.5/1.25/2/1	13,900	11,900	1.24	0.4

^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): δ = 7.88 (d, 2H, H—Ph, J = 9.0 Hz), 7.83 (s, 1H), 7.73 (m, 2H, H—Ph), 7.29 (m, 2H, H—Ph), 6.83 (d, 2H, H-Ph, J = 9.0 Hz), 6.30 (s, 1H, CH_2=, J = 1.4 Hz), 5.93 (d, 1H, CH_2=, J = 1.4 Hz), 3.03 (s, 6H, CH_3—N), 2.02 (s, 3H, CH_3—C). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 165.2, 151.7, 150.2, 143.1, 135.2, 132.6, 131.1, 127.9, 126.1, 122.5, 120.8, 119.2, 111.6, 101.5, 39.9, 18.0. HRMS (m/z): calcd for $C_{21}H_{20}N_2O_2$, 333.1525, found, 333.1601 $[M+H]^+$.

Synthesis of Poly(NIPMAM$_m$-*co*-CPMA$_n$) ($m/n = 250/1$, PCN250)

A Schlenk tube was filled with NIPMAM 316 mg (2.5 mmol), CPMA 3.3 mg (0.0099 mmol), 2,2-azobisisobutyronitrile (AIBN) 1.3 mg (0.0080 mmol), cumyl dithiobenzoate (CDB) 4.3 mg (0.016 mmol), and Nmethylpyrrolidone (NMP) 2.4 mL as solvent. The Schlenk was sealed and the solution was degassed by the freeze–pump–thaw method for three times to remove the oxygen thoroughly. Then, the Schlenk tube was placed in oil bath of 70 °C to begin polymerization. After 36 h, the tube was immerged in liquid nitrogen to quench the polymerization and then opened. The copolymer was purified by precipitating twice from tetrahydrofuran (THF) to diethyl ester, and once from NMP to a mixture of diethyl ether/methanol (1:1, v/v). After being filtrated and dried in a vacuum oven at 50 °C overnight, gray copolymer PCN250 was lastly obtained (223 mg, yield 68.8%), with the number-average molecular mass M_n of 11,900 g/mol and polydispersity M_w/M_n of 1.24.

Synthesis of Poly(NIPMAM$_m$-*co*-CPMA$_n$) ($m/n = 51/1$, PCN51)

The copolymer PCN51 was prepared using the same procedure as that of PCN250. Determined by GPC, the number-average molecular weight of PCN51 is M_n = 11,500 g/mol, with the polydispersity of $M_w/M_n = 1.29$.

RESULTS AND DISCUSSION

Design and Synthesis

The fluorescent unit CPMA is depicted in Scheme 1. DMPHA was functionalized with methacryloylchloride to gain the corresponding monomer CPMA. In ^{1}H NMR of DMPHA and CPMA, the characteristic chemical shift of alkene protons is indicative of the predominant trans-isomer. Finally, the copolymer was prepared by RAFT copolymerization.

As a derivative of DMPHA ((*Z*)-3-(4-(dimethyl-amino)-phenyl)-2-(4-hydroxy-phenyl)acrylonitrile), the monomer of CPMA is also a typical donor–π-acceptor (D–π-A) structure with a broad absorption band resulting from an ultrafast process of intramolecular charge transfer (ICT). Actually, the ICT mechanism of DMPHA derivatives has been exploited for pH sensing and molecular switching.[37] Along with increasing solvent polarity, the dipole–dipole forces in the system of DMPHA derivatives become stronger, thus resulting in a larger charge transfer from the donor moiety of an amino group to the acceptor moiety of a DPAC ((*Z*)-2, 3-diphenylacrylonitrile) group. Consequently, the fluorescence quantum yield of CPMA is dramatically dependent upon solvent polarity. In addition, PNIPMAM is a well-known member of thermo-responsive polymer with a characteristic LCST. The homopolymer of NIPMAM exhibits a coil-to-globule thermoreversible phase transition in dilute aqueous solution and has a LCST at about 46 °C.[38,39] Taken into account in poly(NIPMAM$_m$-*co*-CPMA$_n$), the unit of NIPMAM is incorporated as a thermo-responsive function, labeled with the moiety of DMPHA as solvent polarity and pH sensing unit.

The copolymers were prepared by RAFT polymerization of CPMA and NIPMAM at different molar ratio in the solution of anhydrous *N*-methyl-2-pyrrolidone with CDB as the chain transfer agent and AIBN as an initiator. Determined by GPC, the number-average molecular weight for PCN250 is M_n = 11,900 g/mol ($M_w/M_n = 1.23$), and for PCN51 is M_n = 11,500 g/mol ($M_w/M_n = 1.29$). Both the copolymers' M_n determined by GPC were slightly lower than the calculated values ($M_{n,thoer}$ = 13,900 for PCN250 and 13,000 g/mol for PCN51; See Table 1). The reason for this divergence was due to the calibration of the GPC with respect to polystyrene standards. However, the narrow molecular weight distribution for copolymers PCN250 and PCN51 indicated the control of the polymerization. CPMA was successfully incorporated into the copolymers at approximately content of 0.4% for PCN 250 and 1.9% for PCN51, respectively, as determined by UV/vis spectroscopy (See Table 1 and Supporting Information Fig. S4). Apparently, the molar ratio of CPMA units in the copolymer is much less than that of NIPMAM units so as not to distinctly affect the copolymeric thermosensitivity.

Thermo-Responsive Behaviors

As poly(NIPMAM) contains both hydrophilic amide groups and hydrophobic isopropyl groups on its side chains, most of the polar water molecules can be repelled out of the polymer when heating above the point of LCST,[38–40] thus resulting in the characteristic thermosensitivity. The function of PCN250 as a fluorescence thermometer with pH condition was investigated in a mixture of methanol/water (1/5, v/v) solution. The methanol/water mixture was chosen as solvent system based on the copolymer solubility and fluorescence response to temperature and pH.[22]

As shown in Figure 1(a), the occurrence of a LCST for PCN250 was distinctly observed during heating above 35 °C

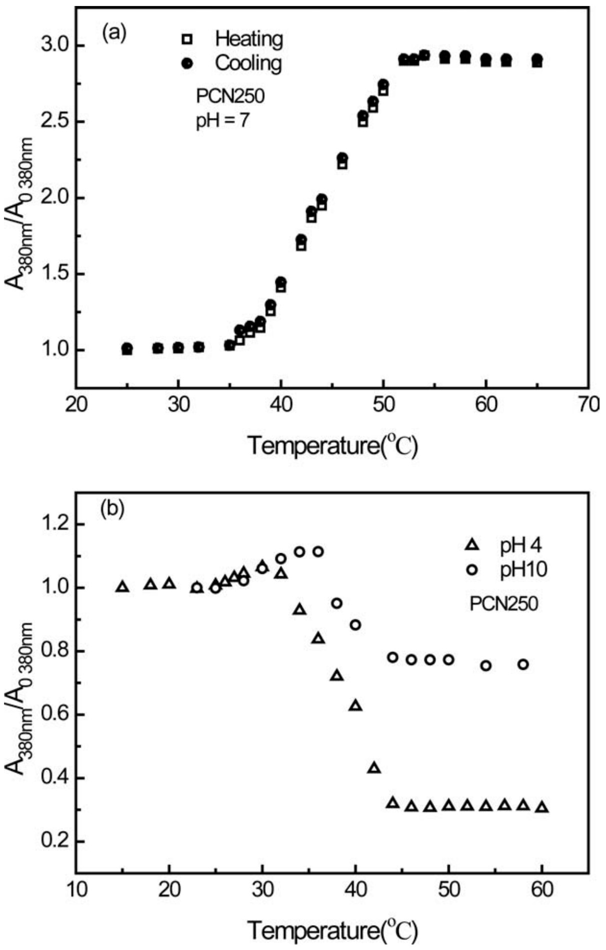


FIGURE 1 (a) Single-run reversibility experiments of the UV/vis absorption responses of PCN250 (1.0 mg/mL) in methanol/water (1/5, v/v) solution at pH 7 to temperature variation at 380 nm. (b) Normalized ratio of absorbance of PCN250 (1.0 mg/mL) at 380 nm in methanol/water (1/5, v/v) solution at various temperatures at pH 4 and 10. HCl and NaOH methanol/water (1/5, v/v) solution (1.0 mol/L) were used for the pH adjustments.

in a solution of methanol/water (1/5, v/v) mixture at pH 7, which is decreased by 11 °C than in aqueous solution due to the addition of methanol.[40,41] However, at pH 4 and 10, the turbidity ($A_{380\ \mathrm{nm}}$) curve of PCN250 is quite different from that of at pH 7 (Fig. 1). It first increases gradually above 25 °C and then decreases drastically above 30 °C at pH 4 and 35 °C at pH 10, respectively. The enhancement of the absorption above 25 °C can be attributed to the copolymer phase transition from coil-to-globule (LCST). While at pH 4, the precipitated polymer particles formed at the temperature of 30 °C, and therefore the turbidity ($A_{380\ \mathrm{nm}}$) curve of PCN250 decreases drastically above 30 °C due to light scattering by the particles [Fig. 1(b)].[42,43] Also at pH 10, the precipitated polymer particles formed above 35 °C and therefore the absorbance of PCN250 at 380 nm decrease above 35 °C because of light scattering of the particles after a slight enhancement upon heating above 25 °C (LCST). Although the thermo-responsive behaviors of PCN250 show similar phenomenon at both acidic (pH = 4) and alkali (pH = 10) environment, it presents less sensitivity of the copolymer to temperature in the alkali environment [Fig. 1(b)]. Additionally, the fluorescent emission of PCN250 shows a hypsochromic shift by about 5 nm upon heating from 35 to 52 °C (Supporting Information Fig. S6) due to the decreased microenvironmental polarity near DMPHA unit.[13,44] Also as a result of the microenvironmental disturbance, the corresponding fluorescence is enhanced to about 1.3-fold [Fig. 2(a)]. More carefully, the fluorescence enhancement was observed in acidic (pH = 4) and alkaline conditions (pH = 10) with an increase of temperature from 35 to 52 °C [Fig. 2(b)]. In addition, the emission intensity of monomer CPMA show obvious temperature dependent change at different pH [Fig. 2(b)]. Consequently, in the system of PCN250, the increase in the microenvironmental hydrophobicity of *N*-alkylacrylamide results in the high sensitivity toward the change in

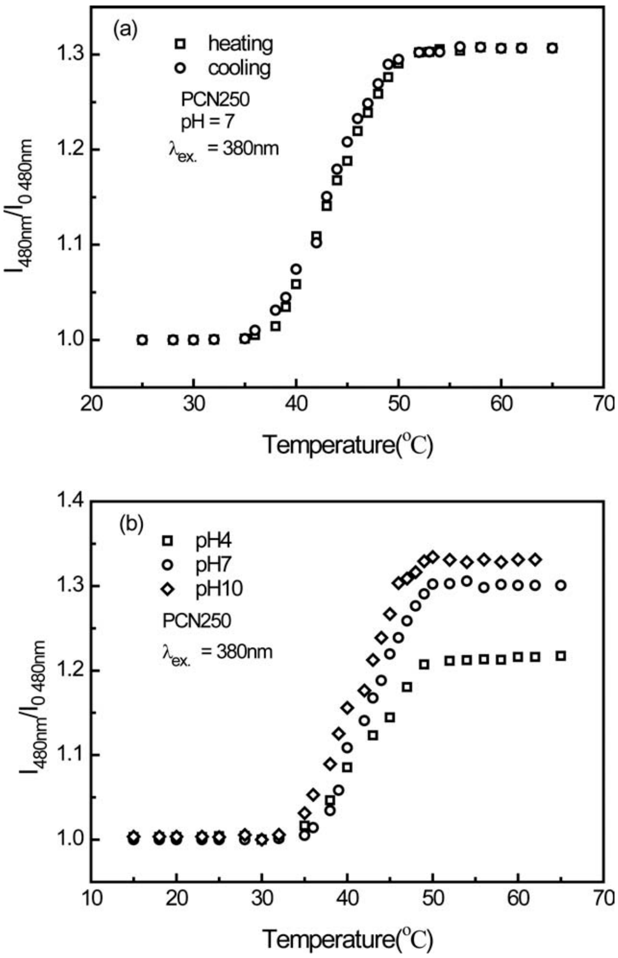


FIGURE 2 (a) Single-run reversibility experiments of the fluorescence responses of PCN250 (1.0 mg/mL) in methanol/water (1/5, v/v) solution at pH 7 to temperature variation at 480 nm. (b) Normalized ratio of fluorescence intensities of PCN250 (1.0 mg/mL) at 480 nm in methanol/water (1/5, v/v) solution at various temperatures at pH 4, 7, and 10. HCl and NaOH methanol/water (1/5, v/v) solution (1.0 mol/L) were used for the pH adjustments.

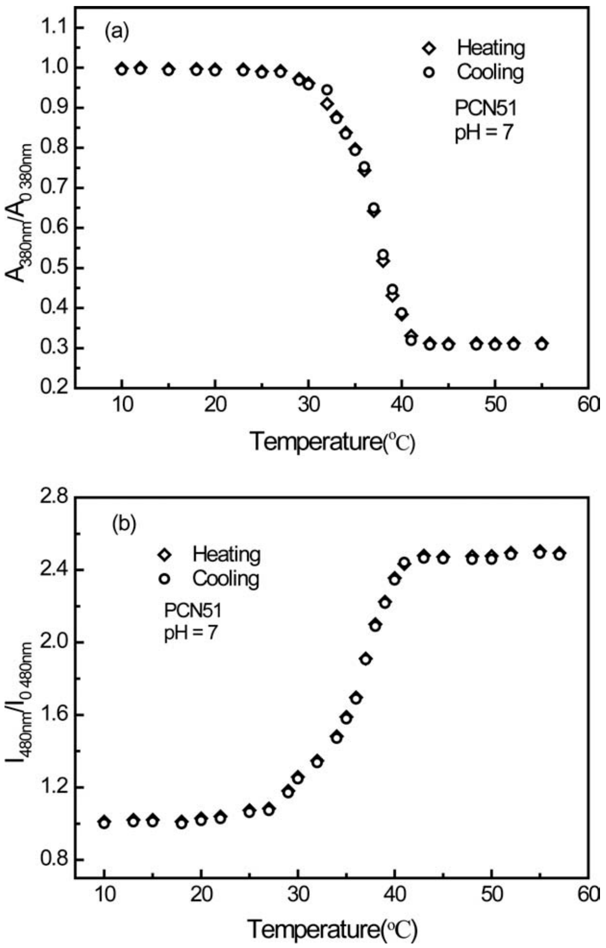


FIGURE 3 (a) Single-run reversibility experiments of the UV/vis absorption responses of PCN51 (1.0 mg/mL) in methanol/water (1/5, v/v) solution at pH 7 to temperature variation at 380 nm. (b) Single-run reversibility experiments of the fluorescence responses of PCN51 (1.0 mg/mL) in methanol/water (1/5, v/v) solution at pH 7 to temperature variation at 480 nm.

temperature at the pH rang of pH = 4.0–10.0 because the copolymer thermosensitivity is dominated by the hydrophobicity/hydrophilicity balance of *N*-alkylacrylamide units. Briefly, the temperature change in the medium plays key role in the ON/OFF switching for the optical and fluorescent copolymeric thermometer at the neutral enviroment.

The LCST values of the copolymers (poly-(NIPMAM$_m$-*co*-CPMA$_n$)) with different component were also investigated. For copolymer PCN51 ($m/n = 51$), the occurrence of LCST was not observed at the experiment conditions. On the contrary, there is significant UV–vis absorption decrease from at temperature above 27 °C in a solution of methanol/water (1/5, v/v) mixture at pH 7, which is very different from that of PCN250 ($m/n = 250$) in methanol/water solution (which shows obvious LCST above 35 °C). For PCN51 solution of 1.0 mg/mL, there is precipitated polymer formed at temperature 27 °C, the significant UV/vis absorption decrease of copolymer (PCN51) above 27 °C can be ascribed to the light scattering by the particles before it can be absorbed by the dye [Fig. 3(a)].[42,43] Therefore, at present concentration of PCN51 solution system, there is no LCST phenomenon observed because of the poor solubility of the copolymer. Additionally, its fluorescent emission shows enhancement upon heating from 27 to 42 °C [Fig. 3(b)], and the corresponding fluorescence is enhanced to about 2.5-fold [Fig. 3(b)]. While the corresponding fluorescence of PCN250 is enhanced only about 1.3-fold upon heating from 35 to 52 °C [Fig. 2(a)], just because of the different content of dye monomer (CPMA) incorporated into the copolymer. Briefly, the different component of the copolymers plays key role in the LCST for the optical and fluorescent copolymeric thermometer.

pH Responsive Behaviors

The optical properties of PCN250 (1.0 mg/mL) are investigated in methanol/water (1/5, v/v) solution. When compared with the absorbance of the monomer CPMA and

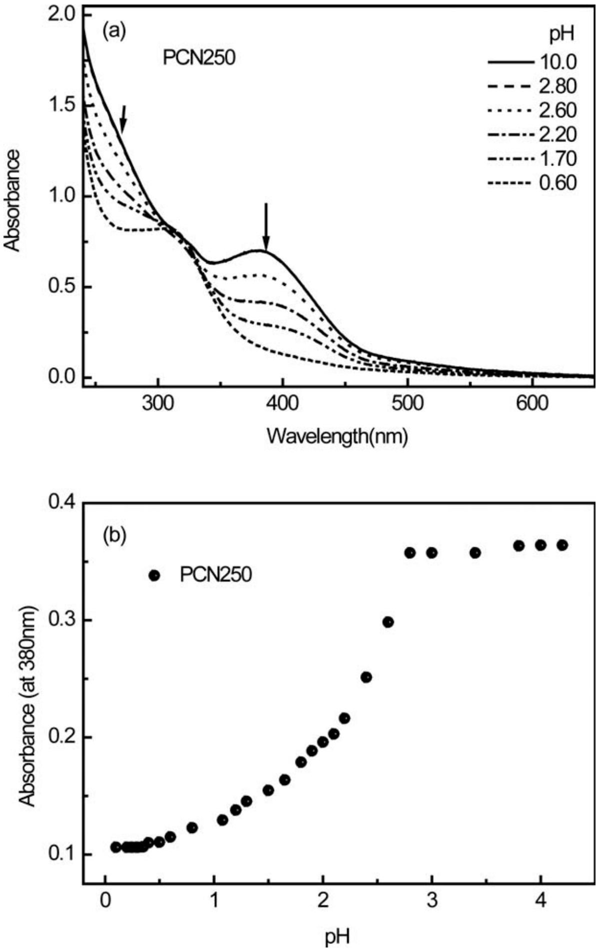


FIGURE 4 (a) UV–vis spectra of PCN250 (1.0 mg/mL) on addition of various concentrations of proton in methanol/water (1/5, v/v) solution at 25 °C. (b) Absorbance at 380 nm versus pH for PCN250 (1.0 mg/mL) in methanol/water (1/5, v/v) solution at 25 °C. HCl and NaOH methanol/water (1/5, v/v) solution were used for the pH adjustments.

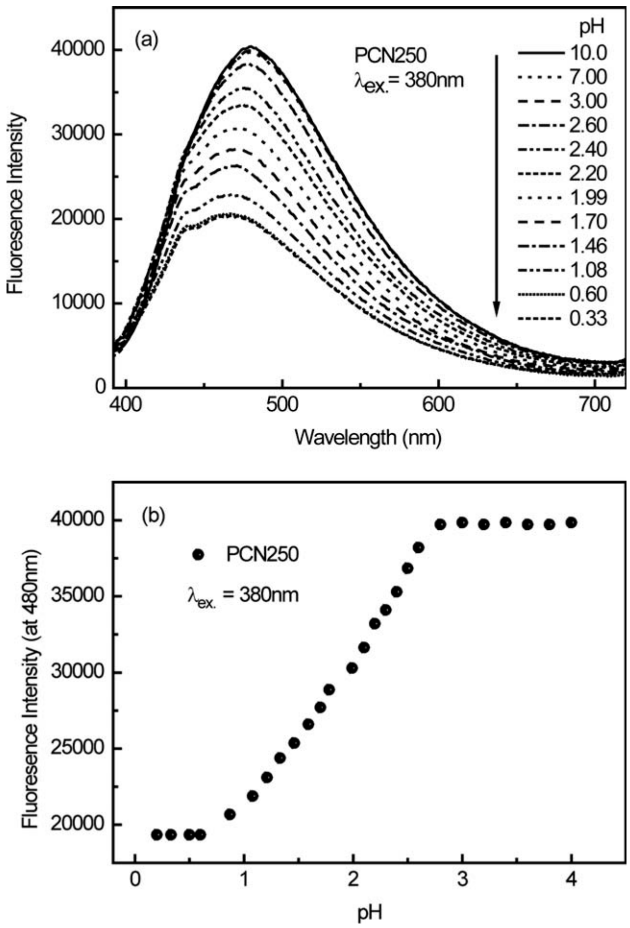
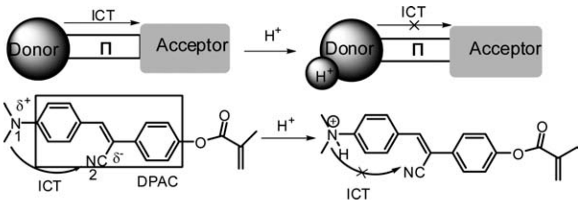


FIGURE 5 (a) Fluorescent spectra of PCN250 (1.0 mg/mL) on addition of various concentrations of proton in methanol/water (1/5, v/v) solution at 25 °C. (b) Fluorescent intensity (excitation wavelength: 380 nm; emission wavelength: 480 nm) versus pH for PCN250 (1.0 mg/mL) in methanol/water (1/5, v/v) solution at 25 °C. HCl and NaOH methanol/water (1/5, v/v) solution were used for the pH adjustments.

copolymer PCN250 in methanol (Supporting Information Fig. S4), they are superimposed to each other, indicating that the characteristic absorption of copolymer poly(NIPMAM$_m$-*co*-CPMA$_n$) is mainly resulted from the CPMA unit. Here, the component of PNIPMAM has no absorbance or fluorescence. Accordingly, the molar ratio (1/250) of monomer CPMA/NIPMAM in copolymer PCN250 was derived from standard absorption working plot.

The PCN250 in methanol/water (1/5, v/v) solution was used to study the pH effect on the absorption and fluorescence properties. When adjusting the methanol/water (1/5, v/v) solution pH from 2.8 to 0.6, the corresponding absorption peak of CPMA unit was remarkable hypochromatic shift with a clear isobestic point at 340 nm (Fig. 4). Notably, the maximum absorbance peak at 380 nm was selected as excitation wavelength. As expected, the fluorescence originating from CPMA unit for PCN250 exhibited good sensitivity to pH in methanol/water (1/5, v/v) solution. Its fluorescence intensity was decreased when changing pH from 2.8 to 0.6, and the peak wavelength shifted little (Fig. 5).



SCHEME 2 ICT (inter charge transfer) process of CPMA before and after in acid.

The fluorescence quench observed in acidic environment can be attributed to the "switching off" process of the ICT process (Scheme 2) from the nitrogen atom (N1) of (dimethylamino)phenyl donor to the DPAC fluorophore through the phenyl ring in the system of PCN250 (Scheme 2). Accordingly, upon decreasing pH, the fluorescence quench can be achieved by the protonation of the nitrogen atom (N1) of (dimethylamino) phenyl unit (Scheme 2).

The effect of proton on fluorescence in thin polymer film of about 10 μm was also investigated. The polymer was immersed in proton solution (pH $=$ 0.6), and after drying for 20 min the fluorescent spectra were monitored, the band at 480 nm dramatically decreased, as can be seen in Figure 6, with quenching effect of 54.5%. The quenching effect could also be observed in the absorbance spectra at 380 nm. On the basis of the present investigation, it can be assumed that the polymer sensors can be made and applied as convenient detecting apparatus for environmental researchers for detection of proton.

CONCLUSIONS

Smart copolymers poly(NIPMAM$_m$-*co*-CPMA$_n$) (PCN250 and PCN51), prepared by RAFT polymerization, have been designed for fluorescent thermometer system based on the hydrophobicity/hydrophilicity balance of copolymer chain and pH sensing. The molecular weights and the monomer

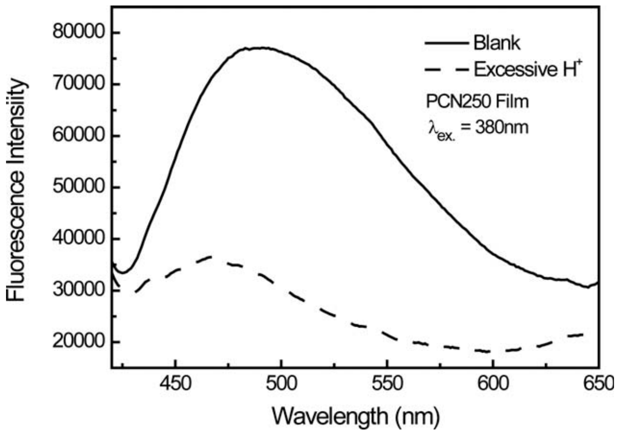


FIGURE 6 Fluorescent spectra of PCN250 thin film processed on quartz.

content copolymer were well controlled by the RAFT method. PCN250 displays specific UV–vis signals when changing the temperature and pH of the copolymer solution in methanol/water (1/5, v/v). When pH is 4 or 10, the absorbance of the copolymer at 380 nm shows selective decrease at a specific temperature range because of the copolymer solubility at these pH values, which cause the precipitation of the polymer and thus results in the light scattering. While at pH = 7, the absorbance of the copolymer at 380 nm presents enhancement when the temperature rises, which indicates the LCST value of the copolymer (LCST 35 °C). However, the fluorescence intensity of this copolymer shows enhancement with a rise in temperature regardless of pH value. This copolymer dissolved in methanol/water (1/5, v/v) solution shows weak fluorescence below 35 °C, while showing fluorescence enhancement above 35 °C and saturation at 52 °C. The fluorescence intensity measured at 52 °C is 1.3-fold higher than that at 35 °C.

Moreover, for copolymers with comparable molecular weights, the thermo-responsive properties of poly(NIPMAM$_m$-*co*-CPMA$_n$) changed with various monomer ratios incorporated in copolymers, that is, with different m/n. When $m/n = 51$ (for PCN51), there is no LCST was observed at the applied solution system. On the contrary, the absorbance of the copolymer PCN51 at 380 nm decreases when the temperature rises from 27 to 42 °C, however, which shows enhancement for PCN250 ($m/n = 250$). However, the copolymer shows fluorescence enhancement with a rise in temperature regardless of PCN51 and PCN250 in different temperature range. In one word, the different component incorporated in the copolymers also plays key role in the LCST for copolymeric thermometers.

What's more, PCN250 ($m/n = 250$) shows fluorescence suppression in the solution with high proton concentration. The pH change in the medium plays a key role in the ON/OFF switching for the fluorescent copolymeric thermometer. Thin PCN250 film also showed fluorescence changes upon addition of proton, which indicates that this copolymer can be made and applied as convenient detecting apparatus for environmental detection of proton.

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