

## Effects of poly-*N*-isopropylacrylamide on fluorescence properties of CdS/Cd(OH)<sub>2</sub> nanoparticles in water

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### ABSTRACT

Effects of poly-*N*-isopropylacrylamide (polyNIPAM) on the fluorescence properties of core/shell type CdS/Cd(OH)<sub>2</sub> nanoparticles (NPs) have been studied in water. The NPs show strong fluorescence at low temperature, but the intensity decreases at >32 °C, allowing an on–off fluorescence switching by temperature. The heat-induced fluorescence quenching is due to the phase transition of polyNIPAM from coil to globule state. The NPs in solution associate with polyNIPAM via a hydrogen bonding interaction. Upon heating the solution, the NPs are confined within the polymer matrices during polymer aggregation. The aggregated polymer suppresses the incident absorption of inner NPs, resulting in fluorescence quenching. A notable feature obtained by the polyNIPAM addition is the enhanced thermal stability of NPs. The NPs confined within the polymer matrices are separated from each other. This therefore suppresses the coalescence of NPs, resulting in high stability even at high temperature.

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### 1. Introduction

There has been much interest in the colloidal semiconductor nanoparticles (NPs) for application to various functional materials, such as biolabeling reagents [1], light-emitting diodes [2], lasers [3], sensors [4], photoelectrochemical cells [5], and photonic crystals [6], because of their unique fluorescent properties derived from the quantum-confinement effects [7]. Much investigation has therefore been devoted to the synthesis of semiconductor NPs with monodispersity and clear surface condition [8]. NPs are, however, unstable especially in water; coalescence of NPs produces larger size particles [1,4]. To improve the stability of NPs, several methods have been proposed such as capping [9] and capsulation methods [10]. Immobilization of NPs onto the polymer supports is one of the methods for this purpose. Three principal methods have been employed for immobilization of NPs onto polymers [11–13]. The first consists of a synthesis of NPs in the presence of polymer containing terminal functional groups, such as thiol, amine, or carboxylic acid (NP growth method) [11]. The second consists of a reaction of NPs with polymer containing terminal functional groups (grafting method) [12]. In both methods, NPs are successfully immobilized onto the polymers via covalent bonding between the terminal functional groups on the polymers with the surface of NPs. The third method consists of a synthesis of polymers in the presence of NPs (polymer

growth method) [13], where NPs are surrounded by the polymer matrices and stabilized. All these methods suppress the coalescence of NPs and, hence, enhance the stability of NPs in water.

Recently, poly-*N*-isopropylacrylamide (polyNIPAM), a thermoresponsive polymer, has been used as the support for NPs [14]. It is well known that polyNIPAM in water shows reversible coil-to-globule phase transition, associated with hydration/dehydration of the polymer chain by temperature [15]. PolyNIPAM is soluble in water at low temperature (coil), but a rise in temperature leads to aggregation of the polymer, leading to the formation of polymer particles (globule) [16]. NPs stabilized with thiol-modified polyNIPAM have been synthesized by the NP growth and the grafting methods [17]. The resulting polymers show temperature-dependent phase transition behavior even in the presence of NPs within the polymer matrices.

Fluorescence behavior of NPs stabilized within polyNIPAM has been studied. Li et al. synthesized CdTe NPs stabilized with cross-linked polyNIPAM hydrogel by the polymer growth method [18], where NPs are surrounded by the polymer matrices and stabilized successfully. The NPs within the polyNIPAM show thermoresponsive fluorescence property; the fluorescence intensity of the NPs is strong at low temperature, but decreases with a rise in temperature due to polymer aggregation. This is because the aggregated polymer absorbs the excitation light and suppresses the photoexcitation of NPs within the polymer. These findings suggest that NPs/polymer hybrid materials have potential for application to thermosensitive devices and sensors. However, in this report [18], aggregation mechanism of the polymer in the presence of NPs, relationship

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between the fluorescence properties and the aggregation behavior, and detailed interaction between NPs and polymer are still unclear.

The purpose of the present work is to clarify the detailed mechanisms of polyNIPAM aggregation, fluorescence behavior of NPs, and interaction between NPs and polyNIPAM, which have not been clarified in the previous work by Li et al. [18]. In the present work, linear polyNIPAM with no terminal functional group was used as support to clarify the detailed interaction between the polyNIPAM chain and the surface of NPs, where core/shell type CdS/Cd(OH)<sub>2</sub> NPs [7a,19] was employed. The NPs show thermosensitive fluorescence behavior; there is strong blue fluorescence at low temperature (<32 °C), but the intensity decreases with a rise in temperature. Absorption, laser scattering, FT-IR, and TEM analyses reveal that the surface of NPs with polyNIPAM associates via a hydrogen bonding interaction and affects strongly the polymer aggregation. We also describe here that the interaction between the NPs and polyNIPAM suppresses the coalescence of NPs and, hence, enhances the thermal stability of NPs.

## 2. Experimental

### 2.1. General

All of the reagents used were of the highest commercial quality and supplied from Sigma–Aldrich and Wako. NIPAM monomer was recrystallized from *n*-hexane prior to use, and the other reagents were used without further purification. Water was used after purification with the Milli Q system followed by argon gas bubbling for 1 h.

#### 2.1.1. Synthesis of core/shell CdS/Cd(OH)<sub>2</sub> NPs

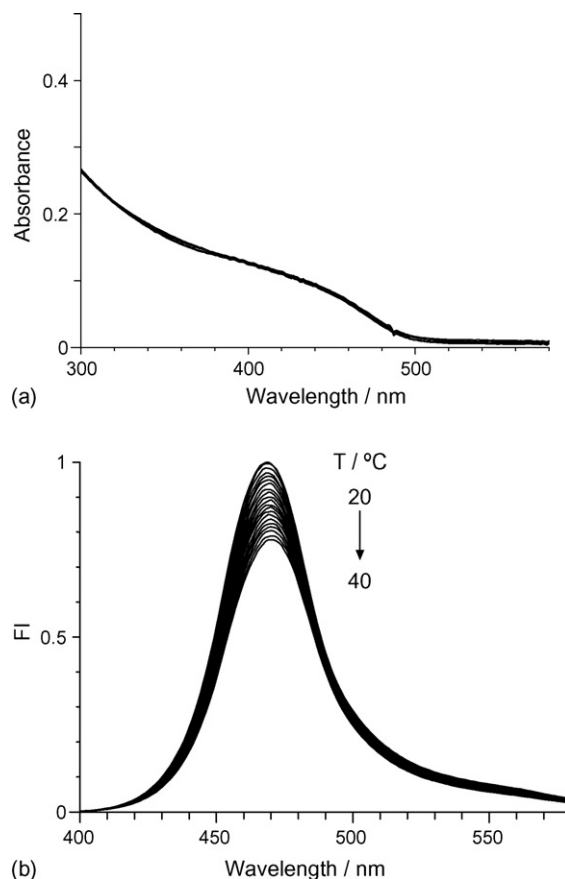
The NPs were synthesized in water according to the literature procedure [7a,19a], as follows: an aqueous Na<sub>2</sub>S solution (0.4 mM, 20 mL) was added rapidly to an aqueous Cd(ClO<sub>4</sub>)<sub>2</sub> solution (0.4 mM, 20 mL) containing 0.2 mM (NaPO<sub>3</sub>)<sub>6</sub>, and stirred at 25 °C for 1 h, affording a yellowish solution containing CdS NPs. NaOH solution (2 M, 50 μL) and Cd(ClO<sub>4</sub>)<sub>2</sub> solution (80 mM, 250 μL) were added to the above solution and stirred at 25 °C for 1 day, affording a yellowish solution (pH 10.8) containing core/shell CdS/Cd(OH)<sub>2</sub> NPs. The diameter of the NPs was determined to be 6.3 nm based on the onset of the absorption spectra [20].

#### 2.1.2. Synthesis of polyNIPAM

PolyNIPAM was synthesized according to the literature procedure [16]. NIPAM monomer (0.61 g, 5.4 mmol) and AIBN (15 mg, 0.088 mmol) were dissolved in *tert*-butanol (4 mL). The solution was degassed by twice freeze–pump–thaw cycles. The solution was stirred at 70 °C for 15 h under dry N<sub>2</sub> and cooled to room temperature. The resultant was concentrated by evaporation and purified by twice precipitation with MeOH (1 mL) and diethyl ether (100 mL). After drying in vacuo, polyNIPAM was obtained as white solid (0.52 g, yield 85%). *M*<sub>n</sub> = 92,793; *M*<sub>w</sub>/*M*<sub>n</sub> = 1.7.

### 2.2. Measurements

Spectroscopic analyses were carried out with a 10 mm path length quartz cell. Fluorescence spectra were measured with magnetic stirring on a fluorescence spectrophotometer (Hitachi; F-4500) with a temperature controller [21]. Absorption spectra were measured with magnetic stirring on an UV–visible photodiode-array spectrophotometer (Shimadzu; Multispec-1500) with a temperature controller (Shimadzu; S-1700) [21]. The measurements were performed after stirring the solution at designated temperature for 2 min. The particle size of NPs and polymers were measured by dynamic laser scattering spectrometer (LB-500, HORIBA) (detection range, 3 nm to 6 μm) and static laser scattering



**Fig. 1.** Temperature-dependent change in (a) absorption and (b) fluorescence spectra ( $\lambda_{\text{exc}} = 300 \text{ nm}$ ) of CdS/Cd(OH)<sub>2</sub> NPs ([CdS] = 0.2 mM) in aqueous solution (pH 10.8) without polyNIPAM.

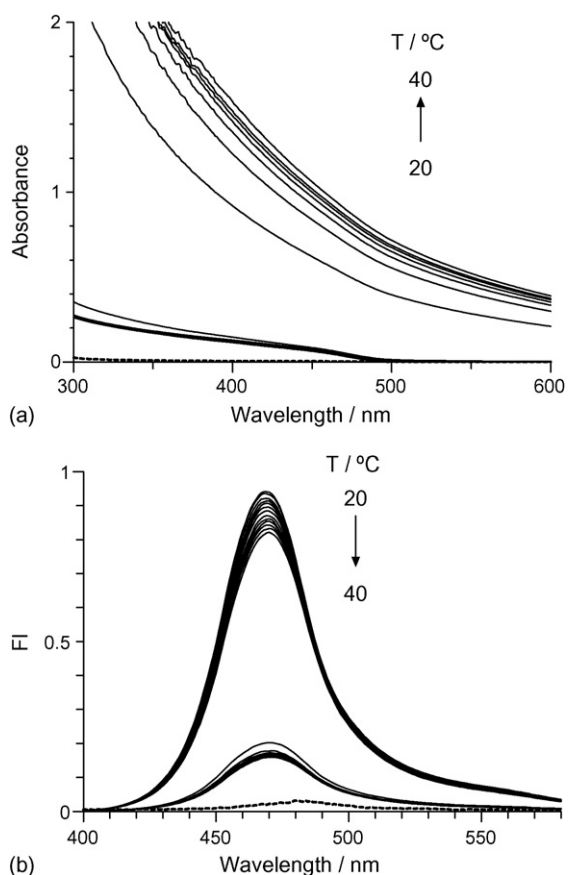
spectrometer (LA-910, HORIBA) (detection range 0.5–700 μm) [22]. Molecular weight of the polymer was determined by Shimadzu SCL-10A Vp GPC system equipped with a LC-10AD Vp pump and a refractive index detector RID-10A using GPC-805 column (Shimadzu). The oven temperature was 40 °C, and THF was used as the carrier solvent (flow rate: 0.6 mL/min) [23]. IR spectra were measured using an FT-IR-610 infrared spectrophotometer (Jasco Corp.) [24]. TEM images were recorded on a JEOL JEM-2010 microscope at an acceleration voltage of 200 kV [25].

## 3. Results and discussion

### 3.1. Fluorescence properties

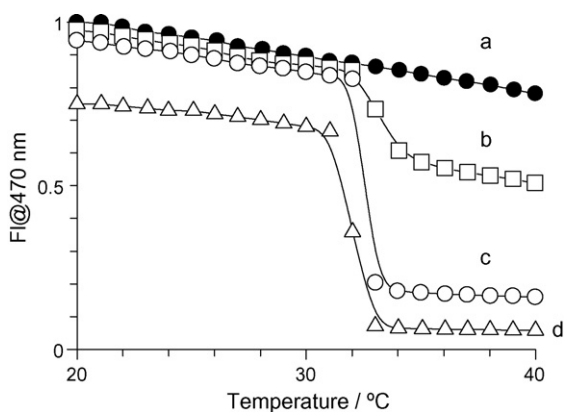
Fig. 1 shows absorption and fluorescence spectra ( $\lambda_{\text{exc}} = 300 \text{ nm}$ ) of NPs measured in aqueous solution (pH 10.8) without polyNIPAM. Distinctive absorption and fluorescence spectra assigned to core/shell CdS/Cd(OH)<sub>2</sub> NPs appear at <500 nm and 400–600 nm, respectively [7a,19]. Excitation spectra collected at  $\lambda_{\text{em}} = 470 \text{ nm}$  are similar to the absorption spectra. In addition, wavelength of the maximum fluorescence intensity is close to the onset of the absorption spectra [7a,19]. These indicate that the 400–600 nm fluorescence is assigned to the bandgap fluorescence of NPs. Fig. 2 shows absorption and fluorescence spectra of NPs measured with polyNIPAM (1.1 g/L). The fluorescence spectra are similar to those obtained without polyNIPAM (Fig. 1b), indicating that NPs also show bandgap fluorescence even in the presence of polyNIPAM.

Fig. 3 shows temperature-dependent change in fluorescence intensity of NP solutions monitored at 470 nm. Without polyNIPAM (a), the intensity decreases gradually with a rise in temperature; the

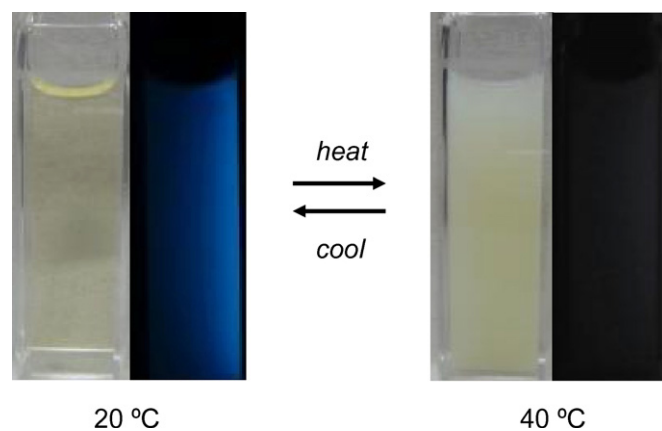


**Fig. 2.** Temperature-dependent change in (a) absorption and (b) fluorescence spectra ( $\lambda_{\text{exc}} = 300 \text{ nm}$ ) of CdS/Cd(OH)<sub>2</sub> NPs ([CdS] = 0.2 mM) measured in aqueous solution (pH 10.8) with polyNIPAM (1.1 g/L). The spectra drawn by dotted lines were measured by following procedure: the NP solution containing polyNIPAM was stirred at 40 °C. The solution was centrifuged (13,000 rpm, 20 min), and the resulting supernatant solution was used for spectroanalysis.

intensity at 40 °C is ca. 85% of that obtained at 20 °C. This intensity decrease is due to the nonradiative hole–electron recombination of the excited state NPs accelerated at higher temperature [26]. With polyNIPAM (b–d), fluorescence intensity decreases drastically at >32 °C, and the decrease occurs more significantly with an increase in the polyNIPAM amount; with 0.11 g/L polyNIPAM (b), the intensity decrease at 30–40 °C is only 40%, whereas addition of >1.1 g/L



**Fig. 3.** Temperature-dependent change in fluorescence intensity ( $\lambda_{\text{exc}} = 300 \text{ nm}$ ) of CdS/Cd(OH)<sub>2</sub> NP solutions ([CdS] = 0.2 mM) measured at  $\lambda_{\text{em}} = 470 \text{ nm}$  (a) without polyNIPAM and with (b) 0.11 g/L, (c) 1.1 g/L, and (d) 11 g/L polyNIPAM. The measurements were carried out during heating sequence. The spectra of NPs measured with 0.11 and 11 g/L polyNIPAM are shown in Figure S1 (Supplementary Material).

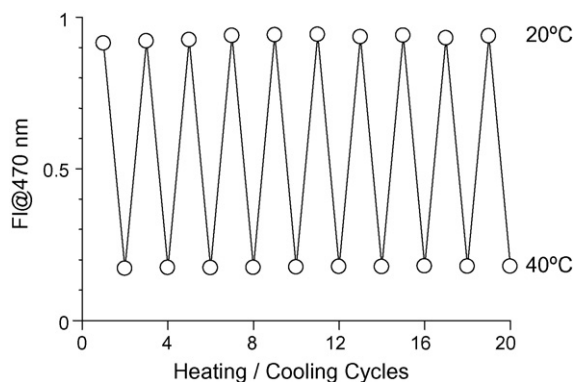


**Fig. 4.** Photographs of an aqueous solution (pH 10.8) containing CdS/Cd(OH)<sub>2</sub> NPs ([CdS] = 0.2 mM) and polyNIPAM (1.1 g/L) taken without or with UV light irradiation at different temperature, where UV light was irradiated from the side of the cell.

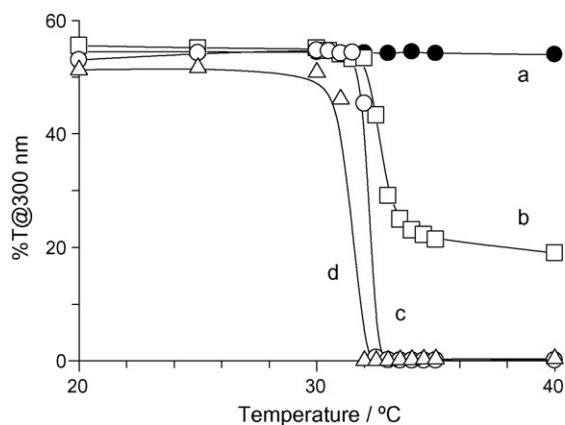
polymer leads to >80% decrease. This suggests that addition of sufficient amount of polyNIPAM allows clear on–off switching of the NP fluorescence. As shown by photographs in Fig. 4, NPs with polyNIPAM show distinctive blue fluorescence at 20 °C, whereas almost no fluorescence is observed at 40 °C. Fig. 5 shows change in fluorescence intensity of NPs with polyNIPAM, where the temperature is changed repeatedly between 20 and 40 °C. The data clearly indicates that the system can change fluorescence intensity reversibly by temperature for at least 10 heating/cooling cycles.

### 3.2. Relationship between the fluorescence properties and polymer aggregation

The on–off fluorescence response of NPs with polyNIPAM is driven by the heat-induced phase transition of polyNIPAM from coil to globule [16]. The fluorescence quenching at >32 °C is due to the formation of globule-state polymer associated with polymer aggregation, leading to suppression of incident light absorption of NPs. Fig. 6 shows temperature-dependent change in transmittance of NP solution measured at 300 nm without and with polyNIPAM. Without polyNIPAM (a), transmittance is almost constant at 20–40 °C. With polyNIPAM (b–d), the transmittance is constant at 20–32 °C, but decreases drastically at >32 °C due to polymer aggregation. The transmittance profiles agree well with the fluorescence intensity profile (Fig. 3). These data clearly suggest that, at >32 °C, NPs in solution cannot absorb the excitation light by polymer aggregation, resulting in fluorescence quenching (Fig. 3).



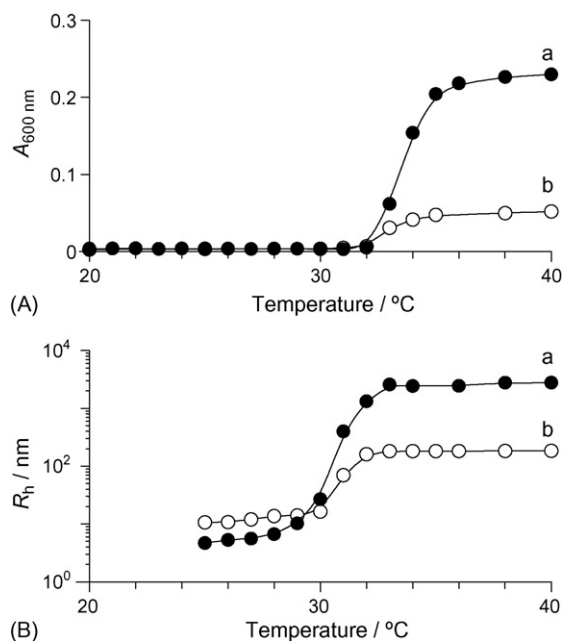
**Fig. 5.** Change in fluorescence intensity of CdS/Cd(OH)<sub>2</sub> NP solution ([CdS] = 0.2 mM) containing polyNIPAM (1.1 g/L) measured at 470 nm during repeated heating/cooling cycles between 20 and 40 °C.



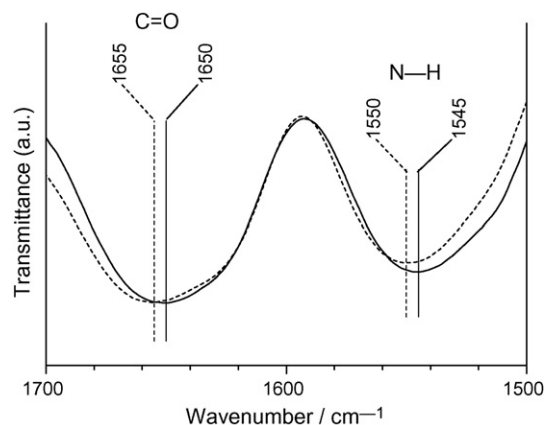
**Fig. 6.** Temperature-dependent change in transmittance of CdS/Cd(OH)<sub>2</sub> NP solution ([CdS]=0.2 mM) measured at 300 nm (a) without polyNIPAM and with (b) 0.11 g/L, (c) 1.1 g/L, and (d) 11 g/L polyNIPAM. The measurements were carried out during heating sequence.

Mechanism of the polymer aggregation was studied in detail. Fig. 7A shows temperature-dependent change in turbidity ( $A_{600\text{ nm}}$ ) of an aqueous solution containing polyNIPAM in the absence and presence of NPs. Without NPs (a), at  $<32^\circ\text{C}$ , the solution turbidity is almost zero. In contrast, at  $>32^\circ\text{C}$ , the turbidity increases drastically, indicating that polymer aggregation occurs at this temperature range [21,22]. Fig. 7B shows change in hydrodynamic radius ( $R_h$ ) of the polymer particles determined by laser scattering analysis. Without NPs (a), polymer particles appear at  $>25^\circ\text{C}$  (detection limit, 3 nm), but the size at  $<30^\circ\text{C}$  is quite small ( $<10\text{ nm}$ ). However, at  $>30^\circ\text{C}$ , the particle size increases drastically and becomes  $2\ \mu\text{m}$  at  $40^\circ\text{C}$ , suggesting that a drastic phase transition takes place at around  $30\text{--}32^\circ\text{C}$ .

Fig. 7A (b) shows the data obtained with NPs. The solution turbidity increases at  $>32^\circ\text{C}$ , which is similar to that obtained without



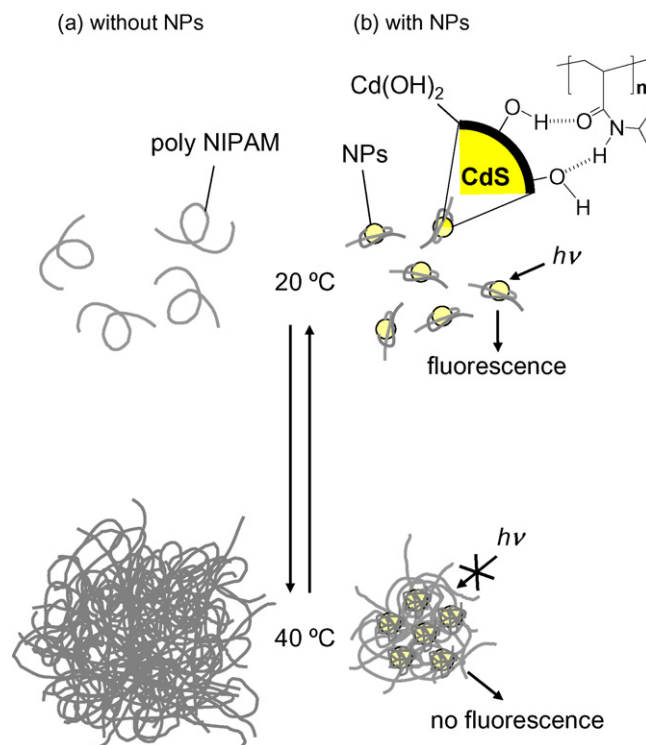
**Fig. 7.** Temperature-dependent change in (A) turbidity ( $A_{600}$ ) and (B) hydrodynamic radius ( $R_h$ ) of the polyNIPAM solutions measured in the (a) absence and (b) presence of CdS/Cd(OH)<sub>2</sub> NPs ([CdS]=0.2 mM). The polyNIPAM amount in solution is 0.11 g/L, and pH of the solution is 10.8. The detailed  $R_h$  distribution data in the absence and presence of NPs are shown in Figures S2 and S3, respectively (Supplementary Material).



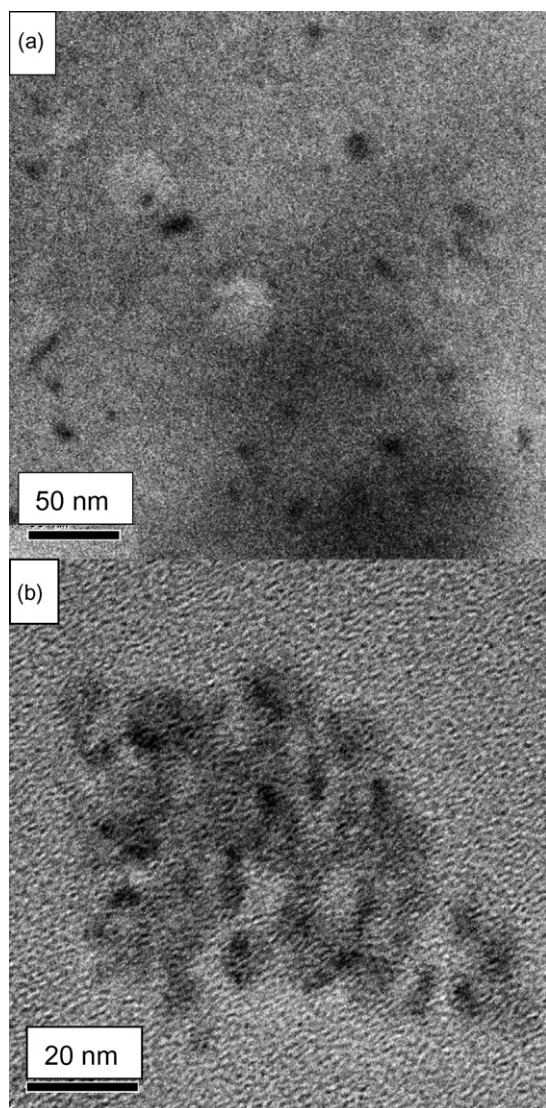
**Fig. 8.** IR spectra of polyNIPAM measured (solid line) without and (dotted line) with NPs.

NPs (a). However, the turbidity is much smaller than that obtained without NPs. As shown in Fig. 7B (b), polymer particle size increases at  $>30^\circ\text{C}$ , as is the case without NPs (a). However, the particle size at high temperature is much smaller than that obtained without NPs (a); the size at  $40^\circ\text{C}$  is 185 nm, whereas the absence of NPs produces  $2\ \mu\text{m}$  particles. These indicate that the presence of NPs suppresses the polyNIPAM aggregation and produce smaller polymer particles. The surface of NPs has hydrophilic nature due to the Cd(OH)<sub>2</sub> shell. As reported [27], polyNIPAM aggregation is suppressed in the presence of hydrophilic groups within the polymer. These imply that association of polyNIPAM with the NP surface may make the polyNIPAM hydrophilic and, hence, suppress polyNIPAM aggregation.

The surface of NPs associates with polyNIPAM via a hydrogen bonding interaction. This is confirmed by IR analysis. As shown in Fig. 8, IR spectra of polyNIPAM measured without NPs (solid

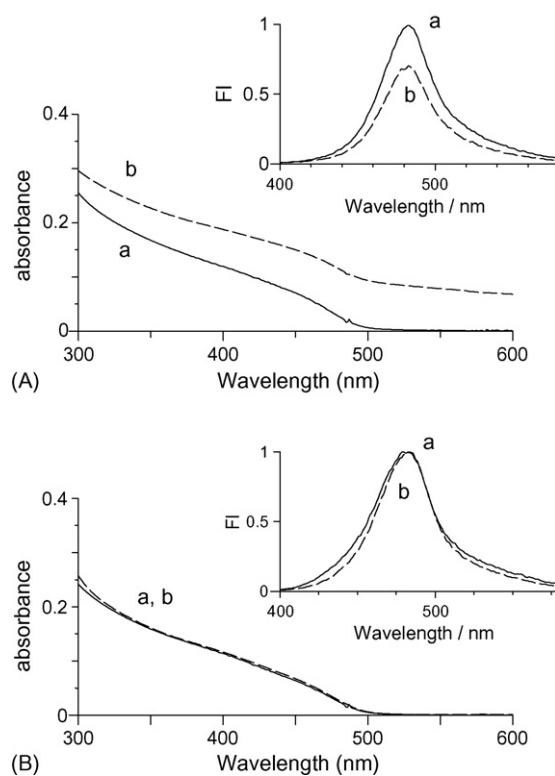


**Fig. 9.** Schematic representation of the aggregation mechanism of polyNIPAM: (a) without and (b) with NPs.



**Fig. 10.** TEM images of CdS/Cd(OH)<sub>2</sub> NPs ([CdS] = 0.2 mM) measured: (a) without and (b) with polyNIPAM (1.1 g/L). The procedure of sample preparation is as follows: for (a), a drop of the solution (25 °C) was put on a sample grid, dried at room temperature for 1 day, and then analyzed. For (b), the solution was heated at 40 °C. The solution was immediately put on a sample grid, dried for 1 day, and then analyzed.

line) show C=O and N–H stretching at 1650 and 1545 cm<sup>-1</sup>, respectively. Addition of NPs leads to shift of the absorption to higher wavenumber (dotted line). As reported [28], solid Cd(OH)<sub>2</sub> interacts with amine or amide groups via hydrogen bonding interaction. The IR data clearly indicate that the NP surface indeed interacts with polyNIPAM via hydrogen bonding interaction. The NP solution containing polyNIPAM was stirred at 40 °C and centrifuged, and the resulting supernatant was used for spectroanalysis. As shown in Fig. 2 (dotted line), the supernatant does not show absorption and fluorescence at 20 °C, meaning that all NPs in solution are confined within the aggregated polyNIPAM and precipitated by centrifugation. In contrast, without polyNIPAM, NPs do not precipitate under the same conditions. Based on these findings, aggregation mechanism of polyNIPAM can be summarized as shown in Fig. 9. With NPs, polyNIPAM associates with the surface of NPs and aggregates around the NPs; therefore, at high temperature, NPs are confined within the polymer aggregate. The confinement of NPs within polyNIPAM aggregate is confirmed by TEM analysis. As shown in Fig. 10a, without polyNIPAM, monodispersed



**Fig. 11.** Absorption and (inset) fluorescence spectra of CdS/Cd(OH)<sub>2</sub> NP solutions ([CdS] = 0.2 mM) measured (A) without polyNIPAM and (B) with polyNIPAM (0.11 g/L) (a) before and (b) after stirring the solution at 40 °C for 5 days. All spectra were recorded at 20 °C.

NPs are observed. In contrast, with polyNIPAM (Fig. 10b), each NP is confined within the polymer aggregate. This supports the proposed aggregation mechanism (Fig. 9b). The heat-induced fluorescence switching mechanism in the presence of polyNIPAM can also be explained (Fig. 9b). At low temperature, polymer aggregation does not occur, resulting in high fluorescence intensity. At high temperature, polymer aggregation around the NPs suppresses the incident light absorption of inner NPs, leading to fluorescence quenching.

It is well known that the NPs in solution tends to aggregate at elevated temperature [9c,26b]. Another notable feature obtained by polyNIPAM addition is the thermal stability of NPs. Fig. 11 shows absorption spectra of NP solution measured without and with polyNIPAM before and after stirring the solution at 40 °C for 5 days. Without polyNIPAM (A), 5 days stirring of the solution at 40 °C leads to increase in the absorbance at >500 nm due to the heat-induced coalescence of NPs [26b]. As shown in inset, the resulting solution shows decreased fluorescence intensity. In contrast, as shown in Fig. 11B, 5 days stirring of the NP solution with polyNIPAM shows almost the same absorption and fluorescence spectra as those obtained before stirring, indicating that the presence of polyNIPAM suppresses the coalescence of NPs even at high temperature. As shown in Fig. 10, NPs in solution associate with polyNIPAM via hydrogen bonding interaction and are confined within the polymer aggregate at high temperature, where NPs are separated from each other by the polymer walls. This suppresses the coalescence of NPs, resulting in high thermal stability. Addition of polyNIPAM to NP solutions allows on–off fluorescence switching by temperature (Fig. 3) and enhances the thermal stability of NPs (Fig. 11). These suggest that NPs/polyNIPAM hybrid materials have potential for application to thermoresponsive soft materials.

#### 4. Conclusion

Effects of polyNIPAM on the fluorescence properties of core/shell type CdS/Cd(OH)<sub>2</sub> NPs in water have been studied. Relationship between the aggregation mechanism of polyNIPAM and the fluorescence properties of NPs was studied by means of absorption, light scattering, FT-IR, and TEM analyses. The surface of NPs associates with polyNIPAM via hydrogen bonding interaction; therefore, the NPs are confined within the polymer particles during polyNIPAM aggregation. The NPs show strong fluorescence at <32 °C, but the intensity decreases at >32 °C, allowing an on-off fluorescence switching by temperature. The fluorescence quenching at high temperature is because the aggregated polymer suppresses the excitation light absorption of inner NPs. The NPs within the polymer aggregate are separated from each other. This suppresses the coalescence of NPs and, hence, enhances the thermal stability of NPs.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.04.001.

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