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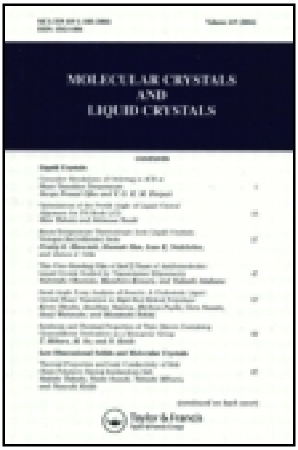

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Temperature-Sensitive Association Properties of End-Functionalized Poly(N-isopropylacrylamide) in Dilute Aqueous Solutions

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Temperature-Sensitive Association Properties of End-Functionalized Poly(*N*-isopropylacrylamide) in Dilute Aqueous Solutions

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It is well known that a thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) becomes turbid above a cloud point (CP) temperature. In this study, the phase transition changes of PNIPAM end-functionalized with pyrenyl group (Py-PNIPAM) were investigated in dilute aqueous solutions. Two types of Py-PNIPAMs were prepared; one is an ester-linkage type (Py-OCO-PNIPAM), and the other an amide-linkage type (Py-NHCO-PNIPAM). From temperature dependence of fluorescence and fluorescence-excitation spectra for these polymer solutions, the micelle-like aggregates formation was found to be more favorable in Py-OCO-PNIPAM. To elucidate the cause of the difference, the partial dipole moments (PDM) of end-pyrenyl groups was obtained by molecular orbital calculations. The PDM value of the ester linkage type was smaller than that of the amide linkage type. The smaller value of PDM in the ester linkage type may explain the reason for the higher ability to form a micelle of Py-OCO-PNIPAM if the pyrenyl groups are assumed to be the core in the micelle.

Keywords: aggregate; excimer; fluorescence; Poly(N-isopropylacrylamide); pyrene

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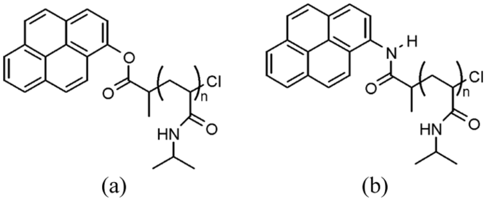
INTRODUCTION

Poly (N-isopropylacrylamide) (PNIPAM) is a typical thermoresponsive polymer that exhibits a coil-globule transition in aqueous solution [1–3] and promising polymeric materials [4]. The thermal response of PNIPAM is expected to be utilized for the application such as enzyme activity control [5], cell sorting [6], molecular filters [7], fluorescent thermometers [8], solid-phase heavy metal extractions [9], and size-exclusion and 'capture release' separations [10]. This phase transition is known to be induced by a conformational change of PNIPAM from the solvated coils below CP to the hydrophobic globular particles above CP. The lower critical solution temperature (LCST), that is defined as the minimum CP of the two-phase curve in the PNIPAM–water phase diagram is typically ca. 32°C. Recently, several authors have reported that synthesis of end-functionalized PNIPAMs for the purpose of the better understanding of the phase-transition mechanism as well as controlling their LCSTs [11–16]. For example, Narumi *et al.* synthesized a series of initiators for the purpose of obtaining well-defined PNIPAMs with different end-groups by Atom Transfer Radical Polymerization (ATRP) [15,16]. Hydrophobic end-groups allowed the formations of PNIPAM micelle-like aggregates below the LCST. This eventually promotes the transition of the PNIPAM chains into insoluble globule forms at a lower temperature. The factors that decrease the LCST are strongly dependent on the structures of the introduced end-groups.

We have previously reported a preparation of pyrene-end-functionalized PNIPAM with an ester linkage (Py-OCO-PNIPAM; Scheme 1(a)) and its thermoresponsive property [16]. The pyrenyl group acted not only as hydrophobic substituent but also as a probe of microscopic association properties of end-functionalized PNIPAM by monitoring the pyrene (Py) excimer fluorescence. According to Winnik *et al.*, the aggregation state of PNIPAM "side"-functionalized with Py was estimated by monomer and excimer emissions of Py in given environments (i.e. micelle, polar solvent, various pH) [17–19]. The observation



SCHEME 1 (a) Py-OCO-PNIPAM and (b) Py-NHCO-PNIPAM.

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of microscopic aggregation environment is of significance in understanding the phase transition behavior, in particular, explaining the fact that end-groups have a great influence on LCST.

In the present study, we prepared pyrene-end-functionalized PNIPAM with an amide linkage (Py-NHCO-PNIPAM; Scheme 1(b)). Dependence of phase transition behavior on concentration and linkage type was investigated by the turbidity and fluorescence measurements for two kinds of end-functionalized PNIPAMs which have different linkages. On the basis of these results, we found that the difference in linkage results in the big difference of their CPs in dilute solutions.

EXPERIMENTAL

Materials and Polymerization

Py-OCO-PNIPAM was polymerized using 1-pyrenyl-2-chloropropianate as the initiator and CuCl/tris [2-(dimethylamino) ethyl]-amine (Me_6TREN) as the catalyst system. The detailed procedure of initiator preparation and polymerization was described elsewhere [16]. Py-NHCO-PNIPAM was polymerized using N-pyrenyl-2-chloropropiamide (PyCP) as the initiator and CuCl/Me_6TREN as the catalyst system. PyCP was prepared by the reaction of 1-amino-pyrene (1.00 g, 4.6 mmol) with 2-chloropropionyl chloride (1.57 g, 15.3 mmol) in dry pyridine solvent under a nitrogen purge at 0°C.

Spectroscopic Measurements

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using a Voyager-DESTR mass spectrometer. UV/VIS absorption and fluorescence spectra were measured with a U-3010 spectrophotometer and F-4500 fluorescence spectrometer, respectively, each of which is equipped with a temperature-regulated cuvette holder. To ensure thermal equilibrium inside a cuvette, each optical measurement was performed waiting 15–20 min after temperature elevation. The temperature inside a cuvette was directly measured with a platinum thermometer. Accuracy of temperature measurements was ±0.5°C. Turbidity was evaluated as transmittance intensity integrated over wavelength region where no optical absorption of the sample was recognized.

Molecular Orbital Calculations

The *ab initio* MO calculations for geometry optimization of monomer models for end-functionalized PNIPAM were carried out using the density functional theory (DFT) method with a B3LYP functional and a 6–31++G (d, p) basis set, which are included in the Gaussian 03 W package [20].

RESULTS AND DISCUSSION

Phase Diagram of Aqueous Py-NHCO- and Py-OCO-PNIPAM Solutions

Figure 1 displays the temperature changes in transmittance based on transmission spectral measurements in aqueous Py-NHCO-PNIPAM and Py-OCO-PNIPAM solutions. Here, CP is defined as the starting point of abrupt decrease in transmittance. By the observation of concentration changes, CP became higher when the polymer

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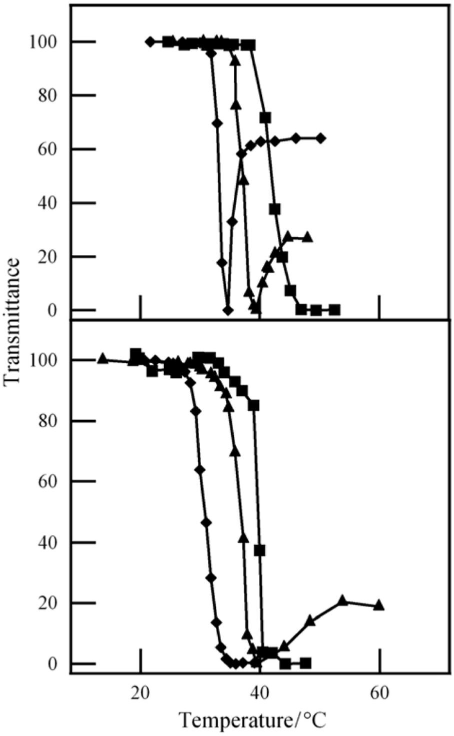

FIGURE 1 Cloud point curves for the aqueous solutions of Py-NHCO-PNIPAM (top) and Py-OCO-PNIPAM (bottom). Square, triangle, and rhombus points were measured at approximately 0.0025 wt%, 0.025 wt%, and 0.10 wt% for both Py-OCO- and Py-NHCO-PNIPAMs, respectively.

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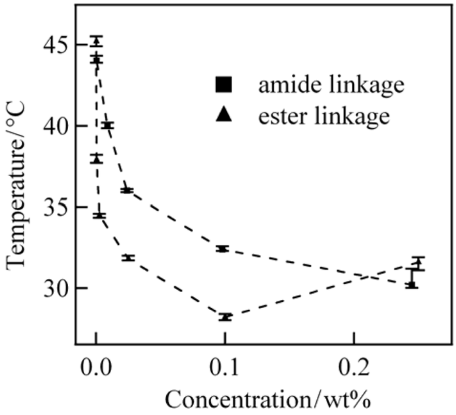

FIGURE 2 Phase diagram of aqueous Py-OCO-PNIPAM ($M_{n,MS} = 5500$, $M_{w,MS} = 6600$, DP = 49) and Py-NHCO-PNIPAM ($M_{n,MS} = 4400$, $M_{w,MS} = 4800$, DP = 39) solutions.

concentration diluted. Additionally, under the same condition of dilute solutions, CP is higher in the amide linkage than in the ester linkage. These concentration dependences of CP in both polymer solutions are shown in Figure 2.

Figure 2 is the phase diagram obtained for Py-NHCO- and Py-OCO-PNIPAM aqueous solutions. Each CP was determined from the optical transmittance or fluorescence measurements. In both curves CP temperature rises when the solutions were much diluted, but the onset of the rise is shifted to dilute region in Py-OCO-PNIPAM than in Py-NHCO-PNIPAM. The modified Flory-Huggins theory that includes hydration effects [21–23] tells us that (1) the CP temperature rises when the polymer solution is diluted, (2) the minimum of CPs shifts to dilute region as the degree of polymerization (DP) of a polymer chain is increased. However, in our case, the DPs were almost the same for measured samples and can not explain the difference observed for CP behavior.

Fluorescence Properties of Aqueous Py-NHCO- and Py-OCO-PNIPAM Solutions

Each fluorescence spectrum of aqueous Py-NHCO- and Py-OCO-PNIPAM solutions below CPs (30°C and 22°C) and above CPs (52°C and 40°C) at lower and higher concentrations is displayed in Figure 3. At higher concentrations, excimer-like fluorescence from pyrene moiety was observed for both polymers above and below CP temperatures;

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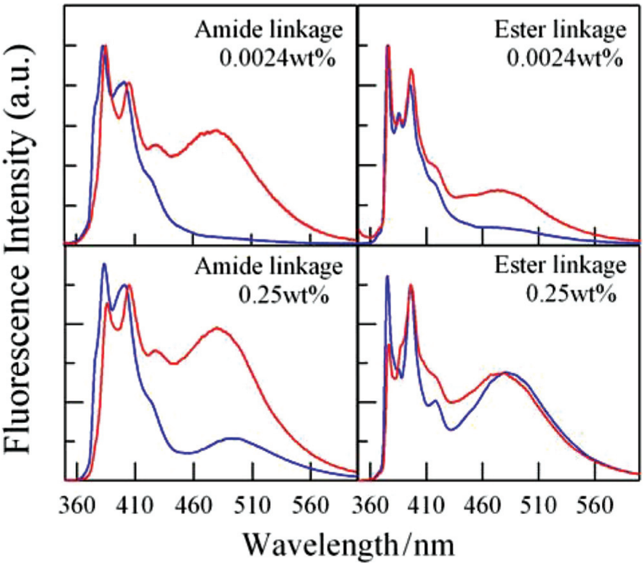

FIGURE 3 Fluorescence spectra of aqueous Py-OCO-PNIPAM (0.0024 wt% and 0.25 wt%) and Py-NHCO-PNIPAM (0.0024 wt% and 0.25 wt%) solutions below CP (blue curves) and above CP (red curves), respectively.

In contrast, at lower concentrations, the excimer-like emission was not observed for Py-NHCO-PNIPAM below CP, although weak excimer-like fluorescence was recognized for Py-OCO-PNIPAM. To explore these fluorescence properties more closely, we measured the fluorescence-excitation spectra at each concentration.

Figure 4 shows fluorescence-excitation spectra of aqueous Py-NHCO- and Py-OCO-PNIPAM solutions at lower concentrations. Above CP, for both the Py-NHCO- and Py-OCO-PNIPAM solutions, the peak positions observed with the excimer-like emission nearly coincided with those observed with the monomer emissions. In contrast, below CP, the peak positions obtained with the excimer-like emission showed a large red shift from those observed with the monomer emission for the Py-OCO-PNIPAM solution. These results suggest that at lower concentrations, only Py-OCO-PNIPAM emitted excimer fluorescence by the direct excitation of the ground-state-dimer below CP. The Py-dimer formation evidenced by fluorescence-excitation spectrum strongly suggests that Py-OCO-PNIPAM forms a micelle below CP at lower concentrations, because Py dimer is stable in hydrophobic environment. Above CP, both the polymers emitted the

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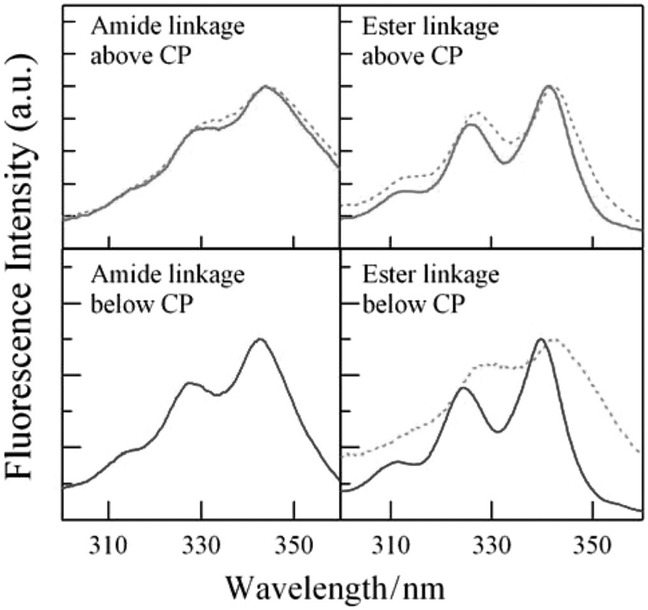

FIGURE 4 Fluorescence excitation spectra of 0.0024 wt% aqueous Py-OCO-PNIPAM and 0.0024 wt% Py-NHCO-PNIPAM solutions below and above CPs. Red (solid line) and orange (dashed line) colored spectra were measured at 52°C with the monomer and excimer emissions, respectively. Blue (solid line) and light-blue (dashed line) colored spectra were measured at 30°C with the monomer and excimer emissions, respectively.

collision-induced excimer fluorescence, suggesting that the polymers in globular states aggregate without forming micelle core above CP at lower concentrations.

Figure 5 shows fluorescence-excitation spectra of the aqueous polymer solutions at higher concentrations above and below CP. Almost no peak shift was observed only for the Py-NHCO-PNIPAM solution above CP, while noticeable peak shifts were observed for the other three cases. On the basis of the fluorescence and fluorescence-excitation spectral measurements and the discussion on the coil-globule transition of PNIPAM main chain, we propose four types of PNIPAM states in aqueous solutions (Fig. 6), which depend on temperature, concentration and the type of the linkage. Py-NHCO-PNIPAMs below CP at lower concentrations exist as single polymer chains (Fig. 6A). Below CP, micelle-like aggregates are formed in both lower and higher concentrations of Py-OCO-PNIPAM solution and in higher concentration region of Py-NHCO-PNIPAM solution (Fig. 6B).

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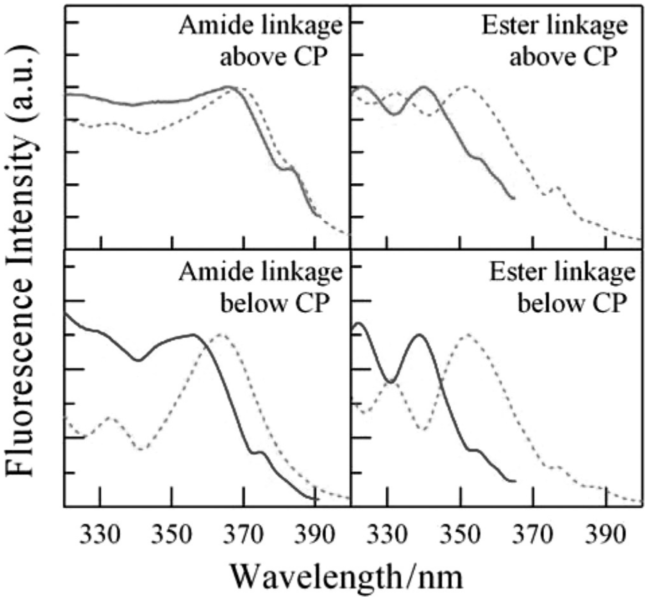

FIGURE 5 Fluorescence excitation spectra of 0.25 wt% aqueous Py-OCO-PNIPAM and 0.25 wt% Py-NHCO-PNIPAM solutions below and above CPs. Red (solid line) and orange (dashed line) colored spectra were measured at 40°C with the monomer and excimer emissions, respectively. Blue (solid line) and light-blue (dashed line) colored spectra were measured at 22°C with the monomer and excimer emissions, respectively.

In the case of Py-NHCO-PNIPAM at higher concentration and Py-OCO-PNIPAM at lower concentration, the micelles dissociate along with the coil-globule transition, and form aggregates of globular states (Fig. 6C). In contrast, micelle changes into the micellar aggregates without dissociation for the case of Py-OCO-PNIPAM solution at higher concentrations (Fig. 6D). These results derived from the fluorescence-excitation spectra suggest that the different concentration dependence between Py-NHCO- and Py-OCO-PNIPAM solutions in the phase diagram (Fig. 2) is due to the difference in micelle-formation ability of the each polymer.

The Dipole Moments of Py-NHCO- and Py-OCO-CH(CH_3)$_2$ Model Compounds

From the DFT calculations, the PDMs were obtained for the optimized structures of each *cis* and *trans* isomers around N-C (O-C) bond in the amide (ester) groups. The PDM values were summarized in Table 1.

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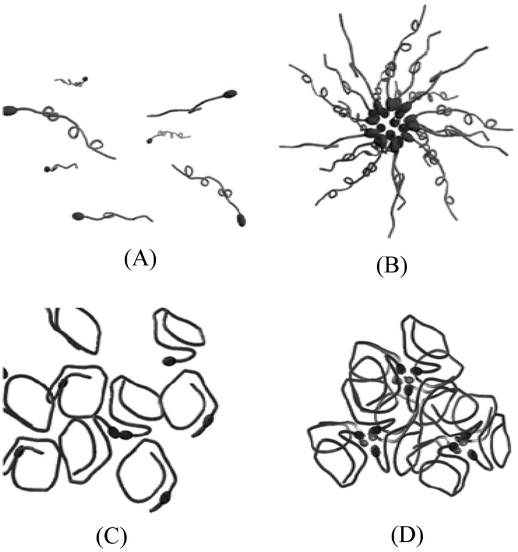

FIGURE 6 Schematic drawings for polymer states; (A) single coiled chain, (B) micelle of coiled states with pyrene core, (C) aggregates of globular states, and (D) micellar aggregate of globular states with pyrene core.

TABLE 1 Partial dipole moments (PDMs) for model compounds

Compounds	PDM/Debye
cis-Py-OCO-CH_3	4.62
trans-Py-OCO-CH_3	1.80
cis-Py-NHCO-CH_3	4.30
trans-Py-NHCO-CH_3	3.18

The interesting finding is that PDM became very small only in the *trans*-Py-OCO compound. This result may explain the reason for the higher ability to form a micelle in aqueous Py-OCO-PNIPAM solutions if Py-OCO-PNIPAM takes the *trans* configuration and form a micelle core.

CONCLUSIONS

We found that the phase transition behavior of Py-OCO-PNIPAM aqueous solution is very different from that of Py-NHCO-PNIPAM aqueous solution by fluorescence spectroscopy. From fluorescence

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measurements, the micelle-like aggregates formation was found to be more favorable in the Py-OCO-PNIPAM solutions. This micelle-like aggregates formation is facilitated by a small dipole moment of the *trans*-Py-OCO group.

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