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Synthesis and thermo-responsive behavior of fluorescent labeled microgel particles based on poly(*N*-isopropylacrylamide) and its related polymers

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Abstract

Poly(*N*-isopropylacrylamide) (PNIPAM) microgel particles labeled with 3-(2-propenyl)-9-(4-*N*,*N*-dimethylaminophenyl)phenanthrene (VDP) as an intramolecular fluorescent probe were prepared by emulsion polymerization. The thermo-responsive behavior of the VDP-labeled PNIPAM microgel particles dispersed in water was studied by turbidimetric and fluorescence analyses. The transition temperature of the VDP-labeled PNIPAM microgel particles in water determined by turbidimetric analysis was ca. 32.5 °C. The wavelength at the maximum fluorescence intensity of the VDP units linked directly to the microgel particles dramatically blue-shifted around the transition temperature. In addition it gradually blue-shifted even below the transition temperature where there was no change observed in the turbidity. These findings suggest that the gradual shrinking of microgel particles occurs with increasing temperature and the subsequent dramatic shrinking results in the increasing in the turbidity. The transition temperatures of VDP-labeled poly(*N*-*n*-propylacrylamide) and poly(*N*-isopropylmethacrylamide) microgel particles determined by turbidimetric analysis were ca. 23 and ca. 42.5 °C, respectively, and their thermo-responsive behavior was similar to that for the VDP-labeled PNIPAM system. In these three systems the microenvironments around the fluorescent probes above the transition temperatures became more hydrophobic than those below the transition temperature, and the estimated values of microenvionmental polarity around the VDP units on their collapsed states were almost the same.

Keywords: Poly(*N*-isopropylacrylamide); Microgel particle; Fluorescent labeled hydrogel

1. Introduction

Stimuli-responsive hydrogels have attracted a widespread interest in the past decade. These materials can change their volumes in response to changes of environments, such as temperature, pH, and concentration of additives. Poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel is one of the most frequent studied temperature-responsive hydrogels [1]. Below the volume phase transition temperature (ca. 34 °C) PNIPAM hydrogels contain more water and they are in a swollen state, whereas at higher temperature they contain less water and they are in a collapsed state [2]. In 1986, Pelton and Chibante first reported the synthesis of PNIPAM microgel particles by surfactant free emulsion polymerization (SFEP) of *N*-isopropylacrylamide (NIPAM) in water at 70 °C in the presence of *N*,*N*′-methylenebisacrylamide (MBAM) as a crosslinker [3]. Since then PNIPAM microgel particles have attracted much attention and their volume phase transition in water has been studied using light scattering, turbidimetric analysis, differential scanning calorimetry, ^{1}H NMR and so on [4–7]. The size of a microgel is much smaller than that of a macroscopic gel (macrogel), so the microgels respond to the external stimuli more quickly than the macrogel and could be useful for practical applications. However, the changes in the local environment inside the microgel particles are less studied.

Fluorescence methods have been widely used in the study of macromolecules and micelles [8]. There are two kinds of fluorescence methods, which have been applied to the investigations for polymer systems; (1) to add a free fluorescent probe to the system and (2) to covalently label the fluorescent probe to the polymer. It was reported by some groups using the former method that the surface or interior of the PNIPAM microgel particles becomes

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hydrophobic in conjunction with its volume phase transition with increasing temperature above the transition temperature [9–12]. However, the fluorescent probes can be located in somewhere inside or surface of the microgel or bulk layer with this method. They are fixed to the polymer chain by labeling the probe to the microgel particles. Therefore, the microenvironment around the main chain could be investigated. Previous works from this laboratory have shown temperature-induced phase transitions of poly(acrylamide) derivatives such as PNIPAM in aqueous solution and their macroscopic hydrogels [13–17]. One of the fluorescent probes that we have used is 9-(4-*N*,*N*-dimethylaminophenyl)phenanthrene (DMA-Phen: DP) in which an electron donor *N*,*N*-dimethylaniline (DMA) and an electron acceptor phenanthrene (Phen) are linked directly with a single bond. DP shows an intense and structureless intramolecular charge-transfer (ICT) fluorescence and its fluorescence emits a strong solvatochromism [18–20]. It could be possible to investigate the thermo-responsive behavior and the microenvironments of the microgel particles by monitoring the fluorescence from the DP units linked to those.

In this study, using a DP derivative, 3-(2-propenyl)-9-(4-*N*,*N*-dimethylaminophenyl)phenanthrene (VDP) (chemical structure is shown in Fig. 1), we synthesized VDP-labeled PNIPAM microgel particles (chemical structure is shown in Fig. 1) using sodium dodecyl sulfate (SDS) as an emulsifying agent to dissolve VDP which is insoluble in water, and studied the thermo-responsive behavior and the microenvironments of the microgel particles dispersed in water. Then the microenvironment of the microgel particles was compared to those of the corresponding linear polymer and macrogel systems in water. The thermo-responsive behavior and the microenvironments of VDP-labeled poly(*N*-*n*-propylacrylamide) and poly(*N*-isopropylmethacrylamide) microgel particles in water were also investigated.

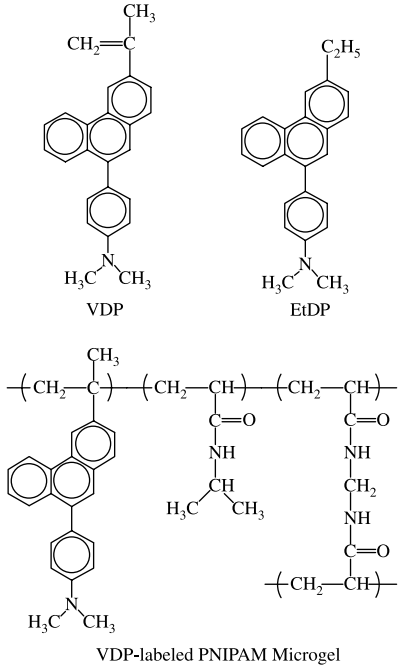

Fig. 1. Chemical structures of VDP, EtDP, and VDP-labeled PNIPAM microgel.

2. Experimental section

2.1. Materials and preparation of microgel particles

NIPAM, *N*,*N*′-methylenebisacrylamide (MBAM), ammonium persulfate (APS), and methanol were purchased from Wako Pure Chemicals. SDS was purchased from Nacalai Tesque. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was purchased from Tokyo Kasei Kogyo. NIPAM was twice recrystallized from *n*-hexane, other chemicals were used without further purification. *N*-*n*-Propylacrylamide (NNPAM) and *N*-isopropylmethacrylamide (NIPMAM) were synthesized and purified as described in the preceding paper [15]. A fluorescent probe monomer VDP and a VDP unit model compound EtDP were the same used in the literatures [13,14]. VDP was synthesized by the Wittig reaction of 3-acetyl-9-(4-*N*,*N*-dimethylaminophenyl)phenanthrene, which was obtained by the Grignard coupling reaction of 3-acetyl-9-bromophenanthrene and (4-(*N*,*N*-dimethylamino)phenyl)magnesium bromide similar to the DP synthesis [18], with methyltriphenylphosphonium bromide and *n*-butyllithium in dry THF. A VDP unit model compound 3-ethyl-9-(4-*N*,*N*-dimethylaminophenyl)phenanthrene (EtDP)(chemical structure is shown in Fig. 1) was obtained by the Wolff–Kishner reduction of 3-acetyl-9-(4-*N*,*N*-dimethylaminophenyl)phenanthrene. Water and methanol used in all experiments were distilled.

All microgel particles were prepared by emulsion polymerization. All preparations were conducted in a 50 mL glass polymerization reactor fitted with a stirring rod with a paddle, and a nitrogen bubbling tube. The reactor was immersed in a water bath set at 70 °C. A monomer NIPAM (100 mM), a fluorescent probe monomer VDP (0.1 mM), a crosslinker MBAM (1 mM), an accelerator TMEDA (2.9 mM), and varying amount of SDS (8.6–17.2 mM) were dissolved in 20 mL of water. The solution was stirred at 300 rpm for 30 min with nitrogen purge to remove oxygen at 70 °C. 0.15 mL of APS aqueous solution (370 mM) was added to initiate the polymerization and the reaction mixture was stirred for 4 h under nitrogen atmosphere. The reaction mixture was poured into a large amount of water to stop the reaction. After separation of the microgel particles by salting-out technique, the microgel particles precipitated were purified by dialysis using distilled water more than 24 times for 2 weeks until absorption of unreacted monomers and other impurities in the water out of the semipermeable tube could not be detected. After purification, the microgel dispersion was

filtered through a 1-μm pore size membrane filter and then freeze-dried. A summary of the microgel particle preparations under various SDS concentrations is given in Table 1. VDP-labeled PNNPAM and PNIPMAM microgel particles were prepared in a similar manner as above. The abbreviations used for VDP-labeled PNIPAM, PNNPAM, and PNIPMAM microgels are as follows: VDP–PNIPAM [X], VDP–PNNPAM [X], and VDP–PNIPMAM [X] where X means SDS concentration (mM) used in the preparation.

2.2. Measurements

The absorption spectra were measured on a HITACHI U-3200 spectrophotometer at 25 °C. The VDP unit contents of the microgel particle were determined from the absorbance of methanol dispersions (10 mg/3 mL), as compared to EtDP ($\varepsilon = 16{,}100\ M^{-1}cm^{-1}$ at 314 nm) as a model compound.

The diameters of the microgel particles were determined by the images of atomic force microscope (AFM). AFM observation was carried out on a SHIMADZU SPM-9500 J3 scanning probe microscope. For the sample preparation the dried microgels were dispersed in water (0.1 w/v%) at 5 °C overnight, then diluted using distilled water. A few droplets of the dispersion were fixed on a micro slide glass and dried at 60 °C for more than 3 h. Minimum and maximum diameters of the 10 microgel particles were listed in Table 1.

The turbidity of the microgel particles dispersed in water (0.1 w/v%) was calculated from the transmittance at 500 nm using the following Eq. (1) [21].

$$\text{turbidity} = 1 - \text{transmittance} \quad (1)$$

The measurement of transmittance was recorded on a HITACHI U-3200 spectrophotometer employing a recirculating water bath to maintain the sample temperature.

The fluorescence spectra of the microgel particles dispersed in water (0.1 w/v%) were measured on a HITACHI 850 fluorescence spectrophotometer with a thermostatically controlled cell compartment. The excitation wavelength was set at 320 nm to excite VDP unit in microgel particles.

The temperature of the samples was monitored with a chromel–alumel thermocouple temperature probe.

3. Results and discussion

3.1. Preparation and characterization of VDP-labeled PNIPAM microgel particles

All PNIPAM microgel particles were prepared by emulsion polymerization using SDS as an emulsifying agent at 70 °C. This temperature is higher than the transition temperatures of PNIPAM microgel particles (ca. 30–34 °C [4–7]), PNIPAM macrogel (ca. 34 °C [2]), and linear PNIPAM (ca. 32 °C [1]) in water reported previously. Various SDS concentrations above its critical micelle concentration (CMC: 8.6 mM [22]) were employed for the polymerization. In other works, PNIPAM microgel particles were prepared by SFEP ([SDS] = 0 mM [3,9,12,23–26]) or emulsion polymerization ([SDS] ≪ CMC [10,11,27–29]) using ionic initiators in water. The charged polymer chains formed during the polymerization process act as surfactant molecules by providing stability for the growing particles [23] and SDS enhances colloidal stabilization during the nucleation stage [27]. In this study, SDS was used to dissolve VDP in the solution before polymerization. Conditions of VDP-labeled PNIPAM and non-labeled PNIPAM microgel particle preparations and VDP unit contents in the microgels formed are listed in Table 1. Those of VDP–PNNPAM and VDP–PNIPMAM microgel particles are also listed. The VDP unit contents increased with increasing SDS concentration used in the polymerization up to 12.6 mM and decreased above 12.6 mM. The microgel particles prepared with 12.6 mM SDS concentration was used for fluorescence analysis.

The diameters of the microgel particles on their dried states determined by AFM are also listed in Table 1. The

Table 1
Recipes for microgel particle polymerizations

Microgel	[SDS] (mM)[a]	[VDP] (mM)[a]	Yield (%)	VDP unit content (mol%)[b]	Diameter (nm)[c]
VDP–PNIPAM [8.6]	8.6	0.1	96.7	0.019	155–180
VDP–PNIPAM [10.6]	10.6	0.1	81.0	0.029	155–180
VDP–PNIPAM [12.6]	12.6	0.1	96.0	0.046	110–190
VDP–PNIPAM [14.6]	14.6	0.1	80.5	0.044	140–160
VDP–PNIPAM [17.2]	17.2	0.1	93.9	0.027	80–110
PNIPAM [12.6]	12.6	0	80.8	0	150–170
PNIPAM [17.2]	17.2	0	41.4	0	105–115
VDP–PNNPAM [12.6]	12.6	0.1	78.5	0.094	240–270
VDP–PNIPMAM [12.6]	12.6	0.1	66.2	0.060	210–270

[monomer] = 100 mM, [MBAM] = 1 mM, [TMEDA] = 2.9 mM, and [APS] = 2.8 mM.

[a] Concentration on preparation.

[b] Calculated from UV visible absorption data of microgel particles dispersed in methanol, using EtDP ($\varepsilon_{314} = 16{,}100\ M^{-1}\ cm^{-1}$).

[c] Determined by AFM on their dried state.

diameters slightly decreased with increasing SDS concentration used in the polymerization from 8.6 to 17.2 mM. The diameters of VDP-labeled PNIPAM microgel particles on their dried state were similar to those of the corresponding non-labeled PNIPAM microgel particles. Thus labeling VDP units did not affect characteristics of the microgel particles.

3.2. Thermo-responsive behavior of VDP-labeled PNIPAM microgel particles in water

The changes in the turbidity at 500 nm of VDP–PNIPAM microgel particles prepared with various SDS concentrations dispersed in water are shown as a function of temperature in Fig. 2. The turbidity of all the VDP–PNIPAM microgel dispersions dramatically increased above ca. 32 °C upon heating the temperature. These dispersions at elevated temperature had been turbid for more than 12 h and the precipitation could not be observed. The effect of the SDS concentration used in the preparation on turbidity could not be observed. The turbidity of microgel dispersion is determined by the difference in refractive index between the microgel–water macrocomplex and the bulk water [12] and therefore the turbidity reflects the amount of water contained within the interstitial region. Hence when the microgel dispersion is heated, some of the interstitial water is expelled and the volume phase transition occurs, and the difference in refractive index between the shrunk microgel and the bulk water increases. This phenomenon results in the increase in the turbidity. The temperature dependence of the turbidity for VDP–PNIPAM [12.6] microgel particles was similar to that for the corresponding PNIPAM [12.6] microgel particles without VDP units. This means that the small amounts of VDP units do not affect the transition behavior. The transition temperature (Tpt) was determined by the intercept of extrapolated lines from low temperature and from high temperature as shown in Fig. 2. The transition temperatures of all the VDP–PNIPAM microgel particles determined by this method were identically ca. 32.5 °C. In the literatures several groups reported thermo-responsive behavior of PNIPAM microgel particles prepared by SFEP ([SDS] = 0 mM) or emulsion polymerization([SDS] ≪ CMC) measured by some methods such as electrophoresis measurements, turbidimetric analysis, differential scanning calorimetry, laser light scattering, small-angle neutron scattering, and so on. The reported transition temperatures of PNIPAM microgel particles prepared with 1% of MBAM are 30–34 °C [27], 34.3 °C [24], 33.5 °C [28], 32 °C [25], 30–33 °C [29], and 34 °C [11]. We re-determined the transition temperatures from their original data by the method described before. As a result all of the above cases show the similar temperature (ca. 32 °C). It can be concluded that the transition temperature of PNIPAM microgel particles with 1% of crosslinker MBAM is ca. 32 °C.

It was also reported that the transition of PNIPAM microgel particles prepared by SFEP dispersed in water is reversible for both heating and cooling and no hysteresis could be observed [12,24,26], though the hysteresis could be observed for the PNIPAM macrogel [30] and the linear PNIPAM systems [31]. No hysteresis was also observed in the dispersion of VDP–PNIPAM [12.6] microgel particles prepared by emulsion polymerization as shown in Fig. 3. The microgel particle has negative charge and the time to reach equilibrium swelling of the microgel particles is short as the size of the microgel particles is small, therefore hysteresis could not be observed. The transition temperature of the VDP–PNIPAM [12.6] microgel dispersion was independent of the microgel concentration from 0.01 to 0.1 w/v% as shown in Fig. 3.

The fluorescence spectra of the VDP–PNIPAM [12.6] microgel particles dispersed in water are shown in Fig. 4 (inset). The dispersion exhibited a broad intramolecular charge transfer (ICT) emission (380–600 nm) from the VDP

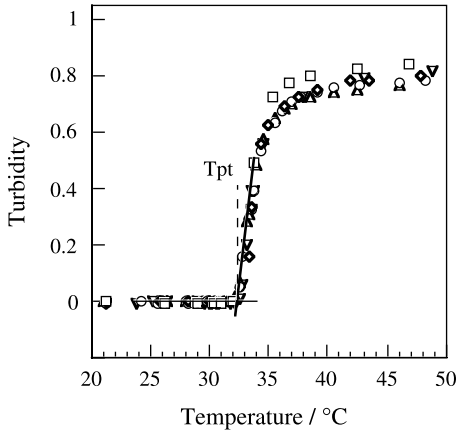

Fig. 2. Turbidity of 0.1 w/v% dispersions of VDP–PNIPAM microgel particles prepared with various SDS concentrations as a function of temperature; [SDS] = 8.6 mM (◇), 10.6 mM (○), 12.6 mM (□), 14.6 mM (△), and 17.2 mM (▽).

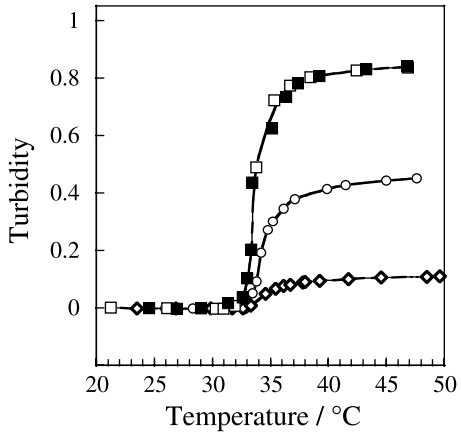

Fig. 3. Turbidity of 0.01 w/v% (◇), 0.05 w/v% (○), and 0.1 w/v% (□, ■) dispersions of VDP–PNIPAM [12.6] microgel particles as a function of temperature upon heating (open symbol) and cooling (full symbol).

units linked directly to the microgel particles. The wavelength at the maximum intensity (λ_{max}) at 40 °C shifted to shorter wavelength compared with that at 25 °C. The λ_{max} value is plotted against temperature in Fig. 4. The λ_{max} blue-shifted with increasing temperature. It dramatically blue-shifted around the transition temperature determined by turbidimetric analysis. As the fluorescence λ_{max} from the VDP units was constant and was not blue-shifted with increasing temperature as previously reported [14], this blue-shift of the λ_{max} reflects an increase of hydrophobicity around the VDP units and the VDP units in the microgel particles can sense and report the deswelling behavior of the microgel particles. As discussed in detail the λ_{max} gradually blue-shifted with increasing temperature from ca. 26 °C (454 nm) to ca. 31 °C (450 nm) where there is no change in the turbidity, and then dramatically blue-shifted from ca. 31 °C (450 nm) to ca. 33 °C (430 nm) where the turbidity increases. The hydrophobicity around the VDP unit gradually increases even below the transition temperature and then dramatically does around the transition temperature. Thus these findings suggest that with increasing temperature a gradual shrinking of microgel particles occurred below the transition temperature, and then a subsequent dramatic shrinking took place. The λ_{max} profile on cooling was the same to that on heating and no hysteresis could be observed.

The changes in the λ_{max} value under repeating measurements of heating and cooling are shown in Fig. 5. The λ_{max} values were 455 nm (relative standard deviation(RSD) ≈ 0%) at 25 °C and 430 nm (RSD = 0.047%) at 40 °C during 10 repetitive experiments. Therefore the thermo-responsive behavior of VDP–PNIPAM [12.6] microgel particles dispersed in water is reversible and highly reproducible.

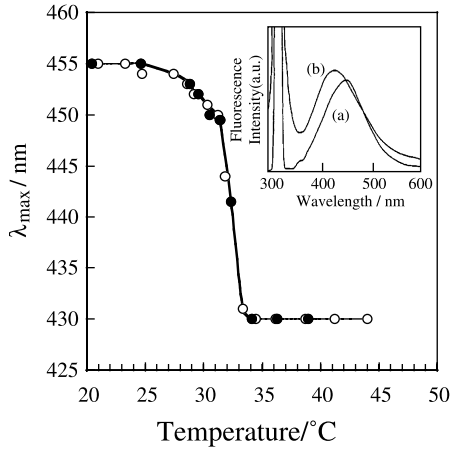

Fig. 4. Fluorescence λ_{max} values of 0.1 w/v% dispersion of VDP–PNIPAM [12.6] microgel particles as a function of temperature upon heating (○) and cooling (●). Inset: Fluorescence spectra of VDP–PNIPAM [12.6] dispersion at 25 °C (a) and at 40 °C (b).

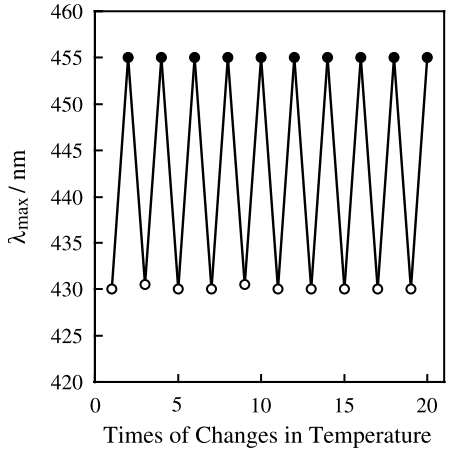

Fig. 5. Fluorescence λ_{max} values of 0.1 w/v% dispersion of VDP–PNIPAM [12.6] as a function of times of changes in temperature between 25 °C (●) and 40 °C (○).

3.3. Thermo-responsive behavior of VDP-labeled PNNPAM and PNIPMAM microgel particles in water

The macroscopic phase separations of aqueous solutions of poly(*N*-*n*-propylacrylamide) (PNNPAM) [32–34] and poly(*N*-isopropylmethacrylamide) (PNIPMAM) [31,32,35,36] are also known. However, there are a few articles of PNNPAM [37] and PNIPMAM microgel particles [38–40]. So we would like to report thermo-responsive behavior of VDP-labeled PNNPAM (VDP–PNNPAM [12.6]) and PNIPMAM (VDP–PNIPMAM [12.6]) microgel particles in water.

The turbidity and the λ_{max} value of the VDP–PNNPAM [12.6] and the VDP–PNIPMAM [12.6] microgel particles dispersed in water are plotted against temperature in Fig. 6. The results of the VDP–PNIPAM [12.6] system are also shown for reference in the figure. The dramatic increase in the turbidity both for the VDP–PNNPAM [12.6] and the VDP–PNIPMAM [12.6] systems similar to the VDP–PNIPAM [12.6] system were observed. The transition temperatures for the VDP–PNNPAM [12.6] and the VDP–PNIPMAM [12.6] systems were ca. 23 and ca. 42.5 °C, respectively. The change in the turbidity for the VDP–PNIPMAM [12.6] system was much broader than that for the VDP–PNIPAM [12.6] system. The NIPMAM unit has a methyl group on the α-carbon, although the NIPAM unit does not. While the changes in the turbidity for the VDP–PNNPAM [12.6] system was sharp as well as the VDP–PNIPAM [12.6] system. The λ_{max} profiles both for the VDP–PNNPAM [12.6] and the VDP–PNIPMAM [12.6] systems were similar to that for the VDP–PNIPAM [12.6] system. The significant changes in the λ_{max} value were observed in the ranges of 21–23 °C (from 449 to 430 nm), 31–33 °C (from 450 to 430 nm), and 42–46 °C (from 452 to 429 nm) for the VDP–PNNPAM [12.6], the VDP–PNIPAM [12.6], and the VDP–PNIPMAM [12.6] systems, respectively. The dramatic change in the λ_{max} value for the VDP–PNIPMAM [12.6] system is greater and occurs over a wider temperature

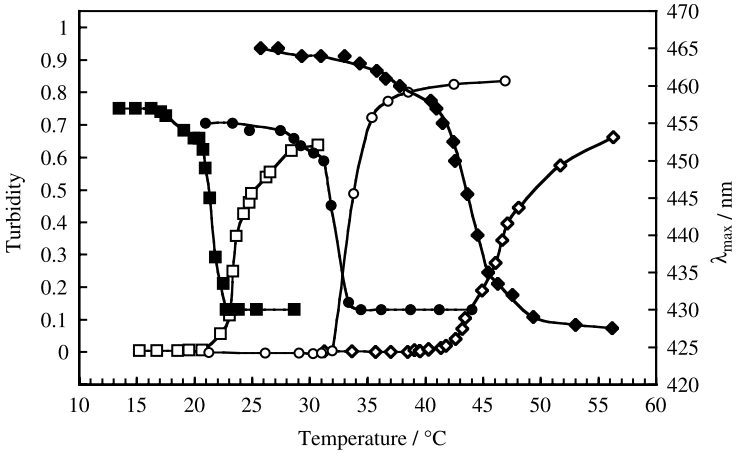

Fig. 6. Turbidity (open symbol) and fluorescence λ_{max} values (full symbol) of 0.1 w/v% dispersions of VDP–PNNPAM [12.6] (□, ■), VDP–PNIPAM [12.6] (○, ●) and VDP-PNIPMAM [12.6] (◇, ◆) microgel particles as a function of temperature.

range than those for the VDP–PNNPAM [12.6] and the VDP–PNIPAM [12.6] systems. These findings suggest that the methyl group on the α-carbon of the NIPMAM unit could attribute to the polymer conformation inside the microgel particles in both the swollen state and the collapsed state. The λ_{max} of the VDP–PNNPAM [12.6] and VDP–PNIPMAM [12.6] slightly blue-shifted even below their transition temperatures where there is no change in turbidity. Thus it was concluded that with increasing temperature a gradual shrinking of the VDP–PNNPAM [12.6] and VDP–PNIPMAM [12.6] microgel particles occurred and then dramatic shrinking took place around their transition temperatures.

3.4. Microenvironments of three kinds of VDP-labeled microgel particles

The relationship between the λ_{max} of a VDP unit model compound EtDP and dielectric constants (ε) of the solvents used is shown in Fig. 7. The λ_{max} strongly responds to the change in the solvents used. As the ε value of the solvent decreased, the λ_{max} blue-shifted from 479 nm (in methanol–water (35/65), $\varepsilon = 62.5$) to 426 nm (in THF, $\varepsilon = 7.58$). Although we have no theoretical explanation, the λ_{max} values were linearly correlated with the solvent polarity. The following Eq. (2) was obtained by least-squares analysis (r value is a correlation coefficient):

$$\lambda_{max}\ (\text{nm}) = 0.9859\varepsilon + 418.24\ (r = 0.998) \quad (2)$$

The microenvironmental polarity near the VDP units in the microgel particles was estimated from the observed λ_{max} value using the Eq. (2) and listed in Table 2.

The estimated ε value for the VDP–PNIPAM [12.6] microgel particles above the transition temperature (at 42 °C, $\varepsilon = 12$) was small as compared to that below the transition temperature (at 22 °C, $\varepsilon = 36$). This means that the hydrophobicity around the VDP units increased with deswelling the microgel particles. The estimated ε values for the VDP–PNIPAM [12.6] microgel system were compared with those for the corresponding linear polymer and macrogel systems in water. Although below their transition temperatures the estimated ε value for the VDP–PNIPAM [12.6] microgel system ($\varepsilon = 36$) was smaller than those for the VDP–PNIPAM macrogel ($\varepsilon = 65$) and linear polymer ($\varepsilon = 64$) systems they were almost the same value among three systems above their transition temperatures ($\varepsilon = 12$, 16, and 16 for microgel, macrogel, and linear polymer systems, respectively). The reason that the estimated ε value for the microgel system is smaller than those for the macrogel and the linear polymer systems seems to be attributed to the different polymerization conditions. Microgel particles are prepared in water at 70 °C and crosslinked on their collapsed state, whereas a macrogel is prepared in DMF-water mixed solvent (2/3, v/v) at 5 °C and crosslinked on its swollen states [14], and a linear polymer is prepared in benzene and it is not crosslinked [13]. Therefore, the water content in microgel particles is

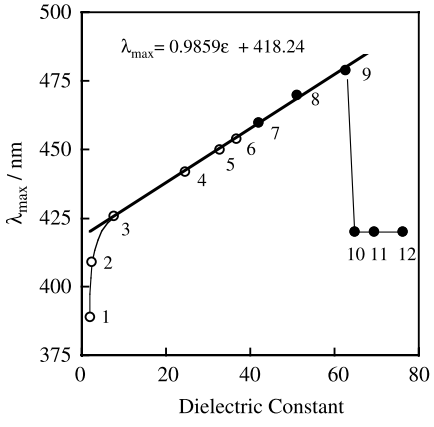

Fig. 7. Plots of fluorescence λ_{max} values for EtDP measured in organic solvents (○) and in methanol–water mixed solvents (●) versus dielectric constant of the solvent. Hexane (1), benzene (2), THF (3), ethanol (4), methanol (5), DMF (6), methanol–water (80/20(7), 60/40(8), 35/65(9), 30/70(10), 20/80(11), and 5/95(12)). The λ_{max} value for (10)–(12) are deviated from others for the aggregates of hydrophobic EtDP.

Table 2
Estimation of the microenvironmental polarities around VDP unit from the maximum emission wavelength of the fluorescent units

System	Tpt[a] (°C)	Tpt[a] − 10 °C		Tpt[a] + 10 °C	
		λ_{max} (nm)	Estimated ε	λ_{max} (nm)	Estimated ε
VDP–PNIPAM [12.6]	32.5	454	36	430	12
VDP–PNIPAM macrogel[b]	34	482[c]	65[c]	434	16
VDP–PNIPAM linear polymer[d]	32	481[e]	64[e]	434[f]	16[f]
VDP–PNNPAM [12.6]	23	457	39	430	12
VDP–PNIPMAM [12.6]	42.5	465	47	428	10

[a] Transition temperature.
[b] Ref. [14]. Preparation condition: [NIPAM] = 700 mM, [MBAM] = 8.6 mM, [VDP] = 0.1 mM, [TMEDA] = 2.7 mM, and [APS] = 0.88 mM in DMF-water mixed solvent (2/3, v/v) at 5 °C for 1 d.
[c] At 15 °C.
[d] Ref. [13]. Preparation condition: [NIPAM] = 1 M, [VDP] = 1 mM, and [AIBN] = 5 mM in benzene at 60 °C for 1 h.
[e] At 25 °C.
[f] At 37 °C.

less than that in the macrogel in their swollen state. Hence the microenvironment around the VDP unit for the microgel particles could be more hydrophobic than those for the macrogel and linear polymer.

The estimated ε values for the VDP–PNNPAM [12.6] and the VDP–PNIPMAM [12.6] microgel systems above the transition temperatures were also smaller than those below their transition temperatures. The microenvironment around the VDP units became more hydrophobic when the transition of those microgel particles occurred. The ε values above the transition temperatures were almost the same value to that for VDP–PNIPAM [12.6] system. Hence the microenvironments around the VDP units for three systems on their collapsed states are similar to each other. Below the transition temperature the ε value for the VDP–PNNPAM [12.6] system was almost the same value to that for the VDP–PNIPAM [12.6] system, however, that for the VDP–PNIPMAM [12.6] system was larger than that for the VDP–PNIPAM [12.6] system. It is reported that linear PNIPMAM in aqueous solution takes a more expanded structure than linear PNIPAM due to the presence of a methyl group to the α-carbon [41]. Similarly PNIPMAM chains in the microgel particles could take more expanded structures than PNIPAM chains. Therefore, the microenvironment around the VDP units for the VDP–PNIPMAM [12.6] microgel particles in their swollen states are more hydrophilic than those for the VDP–PNIPAM [12.6] and VDP–PNNPAM [12.6] microgel particles.

4. Conclusions

VDP-labeled PNIPAM microgel particles were synthesized by emulsion polymerization using SDS. The thermo-responsive behavior of the microgel particles dispersed in water were studied by turbidimetric and fluorescence analyses. The transition temperature of the VDP–PNIPAM microgel particles determined by turbidimetric analysis was ca. 32.5 °C. The fluorescence from the VDP units linked directly to the PNIPAM microgel particles can sense the deswelling behavior of the microgel particles and report the microenvironmental change around the VDP units accompanied by their thermo-responsive behavior. A gradual shrinking of the VDP–PNIPAM [12.6] microgel particles occurred with increasing temperature from 26 to 31 °C, and then subsequent dramatic shrinking took place around 32 °C. The microenvironment around the fluorescent probe becomes hydrophilic in conjunction with the phase transition of the microgel particles. The microenvionment around the VDP units for the VDP–PNIPMAM [12.6] system on their swollen states is more hydrophilic than those for the VDP–PNIPAM [12.6] and the VDP–PNNPAM [12.6] systems, but those on their collapsed state for the VDP–PNIPAM [12.6], the VDP–PNNPAM [12.6], and the VDP–PNIPMAM [12.6] systems are almost the same.

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