Solvation Structure of Polyacrylamide Fine Particle Surfaces Studied by Picosecond Time-resolved Fluorescence Spectroscopy

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Picosecond time-resolved fluorescence measurements using fluorescent probe molecule (C153) were carried out to understand chemical properties around polyacrylamide (PAAm) fine particles. The solvation structure around the PAAm fine particle was investigated by changing the particle size and the length of hydrophilic polymer chains.

Hydrophilic polymer fine particles have unique properties because of their large surface area and hydrophilic polymer chains at the surface. Hydrophilic polymer fine particles have been utilized in many research areas,[1–3] for example, polymer blends, chromatography, polymer-supported catalysis, and drug delivery systems (DDSs). Despite the wide applications of polymer fine particles, there remains much uncertainty regarding influence on natural environments or on the human body. Therefore, fundamental understanding of the chemical properties of fine particles is necessary.

Time-resolved fluorescence spectroscopy is a powerful tool to study molecular dynamics in dilute solution.[4] Moreover, this technique is also applicable to the study of inhomogeneous systems[5] as well as supramolecular assemblies such as micelles and polymers by using fluorescent probe molecules.[6–9] Recently, we synthesize polyacrylamide fine particles (PAAm1), and the chemical properties were investigated by femtosecond and picosecond time-resolved fluorescence spectroscopy using a fluorescent probe molecule (coumarin 153, C153 hereafter).[10] We revealed that the polymer fine particles formed a microscopically unique chemical environment in water solution. In this report, we synthesize another PAAm fine particle (PAAm2) having larger particle size whose hydrophilic polymer chains are shorter than that we reported previously by using a poly(oxyethylene methacrylate) with polymerization number $N = 9$. We investigated how the solvation structure around the PAAm fine particle is different by changing the particle size and the length of hydrophilic polymer chains.

PAAm polymer fine particles (PAAm2) were obtained by dispersion copolymerization of hydrophilic macromonomers (acrylamide, *N*-(hydroxymethyl) acrylamide, 2-hydroxyethyl methacrylate, and acrylic acid) in the presence of AIBN (2,2′-azobis(isobutyronitrile)). Poly(oxyethylene methacrylate) (pOE-MA, $N = 9$) was also introduced as a dispersant, which becomes outer hydrophilic polymer chains. Procedure for the synthesis was described previously.[10] The particle size was evaluated by a SEM and a dynamics light scattering analyzer and the median was 750 nm. Dried PAAm2 (0.1 g) was dissolved in water (100 mL) containing 10 mg of C153. After filtering out the undissolved C153, the filtrate was used for experiments. Picosecond time-resolved fluorescence spectra were measured by a system based on a streak camera. Second harmonics (400 nm, <1 μJ) of a Ti:sapphire laser with a regenerative amplifier (1 kHz) was used as excitation light. The time resolution of this system was estimated to be 20 ps by measuring a streak image of excitation light. Chemical properties around the polymer surface were monitored by the C153 fluorescent probe molecule introduced into the polymer/water solution. All measurements were performed at room temperature.

Picosecond time-resolved fluorescence spectra of C153/PAAm2/H_2O solution are shown in Figure 1. Since C153 is insoluble in bulk water, the steady-state fluorescence spectrum of the C153-saturated/H_2O solution showed only very weak fluorescence at ca. 550 nm. In the presence of PAAm fine particles, on the other hand, solubility of C153 was increased because of hydrophilicity of the polymer particles comparing with that of water. Thus, the C153/PAAm/H_2O solution showed an almost 30-fold increase in fluorescence intensity compared with the C153/H_2O solution. Therefore, time-resolved fluorescence spectra in Figure 1 are assigned to the fluorescence of C153 around the PAAm fine particles. It was observed that the fluorescence peak was ca. 475 nm at delay time origin and that it was red-shifted to 495–500 nm with increasing the delay time. The peak wavelength of the time-resolved fluorescence spectrum at 600 ps was almost the same as that of the steady-state fluorescence (500 nm), indicating that fluorescence peak shift was finished within this delay time. According to the previous works of C153 by Maroncelli and co-workers,[11,12] fluorescence peak shift observed in Figure 1 can be assigned to solvation dynamics around the polymer fine particles. Solvation in Figure 1 can be analyzed quantitatively by using solvation response function, $C(t)$, and the result is shown in Figure 2a. By the fitting analysis two time constants of 18 and 187 ps were derived; however their time constants became shorter than PAAm1 (53 and 467 ps,

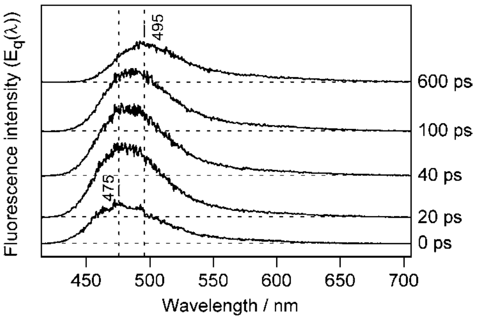

Figure 1. Picosecond time-resolved fluorescence spectra of C153/PAAm2/H_2O solution (excitation 400 nm, <1 μJ). As the delay time was increased, the peak maximum changed from 475 to 495 nm.

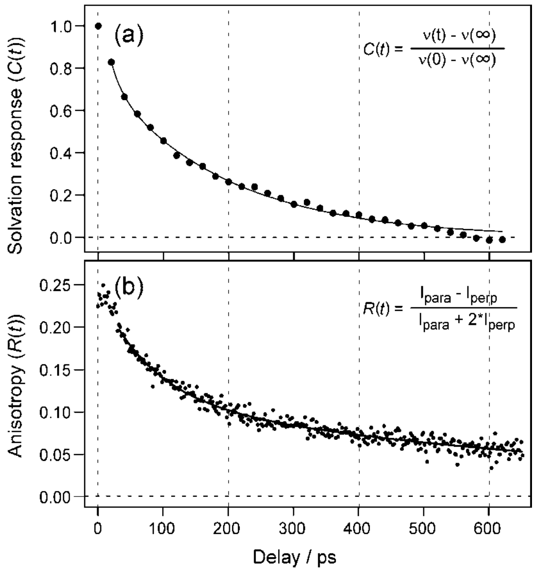

Figure 2. (a) Decay of solvation response function, $C(t)$, of C153/PAAm2/H_2O. The obtained solvation response was analyzed and two time constants, 18 and 187 ps, were evaluated except for the region below the time resolution <20 ps. (b) Anisotropy decays at 500 nm. The anisotropy decayed with two time constants of 80 and 823 ps.

Table 1. Characteristics of PAAm fine particles

Particle	Diameter /nm	Polymerization number of pOE-MA	Fluorescence peak /nm	$C(t)$ /ps	$R(t)$ /ps
PAAm2	750	9	500	18	80
				187	823
PAAm1[a]	500	23	515	53	76
				467	676

[a]Data from Ref. 10.

summarized in Table 1). The reason can be considered as follows: the solvation response function is monitoring the fast reorientation process of polar solvent, water molecules. Water molecules were located in bulk and around hydrophilic polymer chains but not around the hydrophobic core polymers. Therefore, the obtained result of solvation response function mainly contains the information around hydrophilic polymer chains since the solvation of bulk water is finished in very short time period ≈100 fs. We used pOE-MA with polymerization number $N = 9$, and the solvation layer around the polymer particle is thinner than that with $N = 23$ (PAAm1). Therefore, it is considered that the water molecules around the hydrophilic polymer chains were strongly affected by bulk water, and then the solvation response became fast.

As seen from Figure 2a, solvation response function could be reproduced with two exponential functions. However, it has been known that these time constants as well as the number of components do not directly give us the microscopic picture around the particles.[8] To evaluate microscopic properties around PAAm polymer fine particles, rotational diffusion measurements were also carried out. Fluorescence anisotropy was calculated at the peak wavelength of steady-state fluorescence spectrum (500 nm) as the average of the time-resolved fluorescence from 490 to 510 nm, and the result was depicted in Figure 2b. Because of the time resolution of the streak camera, we carried out the fitting analysis in the delay time region of >20 ps, and two time constants of 80 and 823 ps were derived. Comparing the time constants of fluorescence anisotropy with those from the PAAm1 (76 and 676 ps), obtained values became slightly large on the contrary to solvation response function. In the rotational diffusion measurement, we observe the rotational motion of the fluorescent probe molecule (C153). Because of water-insoluble property of C153, the coumarin molecules are selectively located around the polymer particle especially near the core polymer which is considered to be the origin of the less-polar environment of the particles. Therefore, it is considered that the result of fluorescence anisotropy mainly represents the area near the core polymer. Obtained two time constants indicate that there are two different molecular environments around the polymer particles. The rotational diffusion constants were related to microscopic viscosity using the Stokes–Einstein–Debye (SED) equation,[13] and the relation between the rotational diffusion time constant and viscosity can be rewritten as, $\eta_{\rm rot} = \eta_{\rm water}(\tau_{\rm rot}/\tau_{\rm water})$, where $\eta_{\rm water}$ and $\tau_{\rm water}$ are the viscosity of bulk water and the rotation diffusion time of C153 molecules in water, and $\eta_{\rm rot}$ and $\tau_{\rm rot}$ are the viscosity around the polymer surface and the rotational diffusion time. Considering $\tau_{\rm water} \approx$ 67 ps and $\eta_{\rm water} \approx 1$ cP under these experimental condition,[10] $\eta_{\rm rot}$ can be calculated to be 1.2 cP (for 80 ps) and 12 cP (for 823 ps). Compared with our previous work[10] for PAAm1 (1.1 and 11 cP), the viscosity values around the particles were slightly increased because of the increase of surface area of core polymers. Fluorescent probe molecule C153 experiences strong influence from the core, so that it is possible to consider that the hydrophobic environment in water was mainly produced by core polymers and that hydrophilic polymer chains made the polymer particle soluble.

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