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Original Research Paper

Temperature-responsive Pickering foams stabilized by poly(*N*-isopropylacrylamide) nanogels

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ABSTRACT

Poly(*N*-isopropylacrylamide) (PNIPAM) nanogels were synthesized by emulsion polymerization using sodium dodecyl sulfate (SDS). After removal of SDS by dialysis, the surface tensions of the PNIPAM nanogel aqueous dispersions were measured at various temperatures by the pendant-drop method, and it was found that the surface tensions of the nanogel dispersion below the lower critical solution temperature (LCST) of PNIPAM were much smaller than those of water and comparable to those of the SDS aqueous solution. The stability of the aqueous foams generated by nitrogen bubbling thorough the PNIPAM nanogel dispersion was investigated below and above the LCST of PNIPAM. The foam prepared below the LCST was stable in some degree, whereas almost no foam was formed above the LCST. Moreover, the foam prepared below the LCST was quickly collapsed by changing the temperature above the LCST. This rapid defoaming represents that the surface activity of the PNIPAM nanogel can be switched off by the temperature increase across the LCST.

1. Introduction

Amphiphilic molecules such as surfactants and amphiphilic polymers are widely used in various industrial processes since they can adsorb on gas-liquid interfaces to reduce the surface energy, which results in the formation of stable foams [1]. Certain types of fine particles also act as foam stabilizers and have several advantages over surfactants and polymers [2–10]. One of their advantages is that the particulate stabilizers strongly adsorb on liquid surfaces and form stable foams compared with molecular foam stabilizers. However, this can also be disadvantage because the defoaming is sometimes required during practical processes.

To realize the prompt collapse of such Pickering foams, some research groups have developed the stimuli-responsive particulate foam stabilizers in this decade. Binks et al. reported that polystyrene (PS) particles stabilized with poly(acrylic acid) (PAA) can act as a pH-responsive foam stabilizer [11]. In aqueous solutions including the PAA-stabilized PS, stable foams were obtained at low pH, whereas no foam can be prepared at high pH. Moreover, the foam prepared at low pH can be collapsed by increasing the solution pH. Fujii et al. also succeeded in demonstrating that the aqueous foams stabilized by the PS particles carrying poly[2-(dimethylamino) ethyl methacrylate] (PDMA) or poly[2-(diethylamino)ethyl methacrylate] (PDEA) hair exhibit the pH-responsive defoaming [12,13]. The pH-dependence of the stability of the foams prepared with the PDMA-PS and the PDEA-PS particles was opposite to those with the PAA-PS particles. Velev and his co-workers demonstrated that the Pickering foams can be prepared by using the composite of hypromellose phthalate particles and oleic acid-coated carbonyl iron particles, and these foams can be rapidly destroyed by applying a magnetic field [14,15].

These studies suggest that the stimuli-responsiveness is highly effective in the on-demand defoaming. It is well known that poly (*N*-substituted acrylamide)s have the lower critical solution temperatures (LCSTs) and are called as temperature-responsive polymers: poly(*N*-isopropylacrylamide) (PNIPAM) is the most popular among them, and its LCST is around 305 K [16,17]. Although one would expect that the temperature-responsive particulate foam stabilizers can be developed by using such polymers, it is difficult to use them as a particulate foam stabilizer without any modification since they are soluble in water below their LCSTs. Ngai et al. first reported stable oil-in-water emulsions can be prepared by using PNIPAM microgels copolymerized with a cross-linker and methacrylic acid [18]. Following their work on the PNIPAM-based microgels as emulsifier, many studies on the properties of the o/w emulsions stabilized by the PNIPAM-based microgels have been conducted [19–34]. Water-in-oil emulsions stabilized by the

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PNIPAM-based microgels can be also prepared [35,36]. To our knowledge, on the other hand, no study on the foams stabilized by PNIPAM gel particles has been reported to date. In the present article, we have prepared PNIPAM nanogel particles by emulsion polymerization and investigated whether the foams stabilized by the PNIPAM nanogels show the temperature-responsiveness. The surface tensions of the nanogel aqueous dispersion were measured at various temperatures and compared with those of SDS and PNIPAM linear polymer solutions to quantitatively evaluate the surface activity of the PNIPAM nanogels. Next, the stability of the foams prepared in the PNIPAM nanogel dispersion was examined below and above the LCST of PNIPAM.

2. Materials and methods

2.1. Materials

N-Isopropylacrylamide (NIPAM) was kindly supplied by Kojin Co., Ltd. (Tokyo, Japan). *N*,*N*,*N*′,*N*′-Tetramethylethylendiamine (TEMED), *N*,*N*,*N*′,*N*′-methylenebisacrylamide (BIS), sodium dodecyl sulfate (SDS), ammonium persulfate (APS), 2,2′-azobisisobutyronitrile (AIBN) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Deionized and distilled water was used, and all reagents were used as received in the present study.

2.2. Preparation of PNIPAM nanogels and PNIPAM polymer

PNIPAM nanogels were prepared by emulsion polymerization using SDS. NIPAM (40 mmol), BIS (cross-linker, 4.0 mmol), and TEMED (accelerator, 1.2 mol) were dissolved in water (100 mL), and this solution was deoxygenated by nitrogen bubbling for 20 min at 298 K. After addition of SDS (1.0 mmol), the solution was heated up to 333 K and stirred at 200 rpm for 30 min, and then APS (initiator, 0.1 mmol) was added to the solution. The emulsion polymerization was carried out under nitrogen atmosphere with stirring for 2 h. The obtained NIPAM nanogel dispersion was dialyzed against water using a cellulose dialysis membrane (MWCO 50,000) for 1 week to remove SDS from the dispersion. The absence of SDS in the nanogel dispersion after dialysis was confirmed by the measurements of sulfur concentrations using an inductively coupled plasma spectrometer (ICPS-8100, Shimadzu, Japan). The electrophoretic mobility and the hydrodynamic diameters of the PNIPAM nanogels before and after dialysis were measured on an ELSZ-1 (Otsuka Electronics, Japan).

PNIPAM polymer was prepared by free-radical polymerization. NIPAM (20 mmol) and TEMED (0.24 mmol) were dissolved in water (20 mL). The solution was deoxygenated by nitrogen purge, and then APS (0.1 mmol) was added to initiate the polymerization at 298 K with vigorous shaking. After 24 h, water was distilled away, and the residue was dissolved in small amount of ethanol. The concentrated solution was poured into a large volume of *n*-hexane to precipitate the polymer, and the collected polymer was dried under reduced pressure. The molecular weight of PNIPAM was determined by the relationship between the intrinsic viscosity in water and the molecular weight [37,38] and found to be 2.0×10^6.

2.3. Surface tension measurements

The surface tensions of the PNIPAM nanogel dispersion without SDS were investigated at 298–333 K by the pendant-drop method [39]. In the present study, we used the experimental setup shown in Fig. 1, to measure the surface tensions at given temperatures. A needle nozzle (SUS304, outer diameter 1.27 mm, inner diameter 0.88 mm) was vertically fixed through the screw cap of a square glass bottle with an epoxy resin adhesive, and connected to a syringe pump (SPS-1. AS ONE, Japan) through a three-way cock and PTFE tube. This square bottle with the needle nozzle is placed in a water bath with a window (BK300, Yamato Scientific Co., Ltd., Japan) equipped with a low temperature circulator (CTP-1000, EYELA, Japan), and then the PNIPAM nanogel dispersion (10 mM on a monomer basis) was fed by a syringe pump at 0.1 mL h^{-1}. The pendant drop formed at the tip of the needle nozzle was monitored by a CMOS camera (Moticam 2000, Shimadzu, Japan) mounted with a zoom lens (MS-40D, Meiji Techno, Japan). For the pendant drop just before leaving the nozzle tip, the two diameters, d_e and d_s, were measured: d_e is the equatorial diameter and d_s is the diameter in the horizontal plane vertically away from the bottom tip of the drop by a distance d_e, as shown in Fig. 2. By applying these two values to the following equations, the surface tension γ was calculated:

$$\gamma = \frac{g\rho d_e^2}{H} \tag{1a}$$

$$\frac{1}{H} = \frac{0.31968}{(d_s/d_e)^{2.59725}} - 0.11714(d_s/d_e)^2 + 0.50059(d_s/d_e) - 0.13261 \tag{1b}$$

where g is the acceleration of gravity and ρ is the density of the solution. We also measured the surface tensions of water, the SDS aqueous solutions (10 mM), the NIPAM monomer aqueous solutions (10 mM), and the PNIPAM polymer aqueous solutions (10 mM on a monomer basis) for comparison. The above concentration of SDS is higher than the critical micelle concentration of SDS in ambient water, 8.27 mM [40].

2.4. Foam stability test

A 2-mL PNIPAM nanogel dispersion (10 mM on a monomer basis) was added into a test tube (inner diameter 14 mm, height 105 mm), and the tube was put in a water bath at 298 or 333 K, which is below/above the LCST of PNIPAM. To generate foams, a nitrogen gas was flowed into the dispersion through the glass ball filter (pore diameter 5–20 μm) (Kinoshita Rika Kougyou, Japan) at 10 mL/min for 1 min. The foam heights were measured immediately after generated and at certain time intervals. The same tests were conducted using the SDS aqueous solution (10 mM) and the PNIPAM polymer aqueous solution (10 mM). Also, the change of the foam at 333 K was observed, where the foam was generated at 298 K and quickly transferred into a water bath at 333 K. Note that the nanogel concentration in the present study corresponds to 1.13 mg mL^{-1}, which is only a few percent of the values employed in the reported studies on the particle stabilized foams [11–15,41,42].

3. Results and discussion

3.1. Characteristics of PNIPAM nanogel

The hydrodynamic diameter distributions of the PNIPAM nanogels before and after dialysis are shown in Fig. 3, which suggests that the monodisperse nanogels were prepared by the emulsion polymerization. Before and after dialysis, that is, with and without SDS, there was no apparent change in the shape of the distribution, but the size of the nanogels became larger after SDS removal: the average diameters of the PNIPAM nanogels with and without SDS were 43.7 and 48.2 nm, respectively. The PNIPAM nanogel before dialysis is probably more hydrophobic than the nanogel after dialysis because the hydrophobic chains of SDS exist within. This leads to the slight swelling of the PNIPAM nanogels after dialysis.