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Ultrasound Scattering Studies on the Aqueous Suspension of Thermo-sensitive Gel Particles

感熱応答ゲル微粒子懸濁液の超音波散乱解析

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1. Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known thermo-sensitive polymer which undergoes coil-to-globule transition at 32℃. Its polymer gels also show similar transition around 34℃ where PNIPAM microgels contain a large amount of water below the transition temperature, T_c, while the microgels release water above T_c.[1)] Due to the unique property, many applications with PNIPAM are available, for example, biosensing,[2)] catalysis,[3)] and drug delivery systems.[4)] When microgels shrink and release water, the size and mechanical property of microgel change. In the previous works, we measured rigid particles (e.g., silica and polydivinylbenzene) which have a large acoustic impedance difference with a surrounding liquid.[5,6)] In this study, we measured microgels containing a large amount of water by ultrasound upon temperature stimulation.

2. Experimental Procedure

Fig. 1 shows schematic illustration of making microgels. PNIPAM microgels were prepared by a free radical polymerization using Oil-in-Water-in-Oil (O/W/O) emulsion as a template. First, 10 mL of an aqueous solution containing NIPAM, *N*,*N*'-methylenebisacrylamide (BIS-AAm), ammonium persulfate (APS), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TEMED) and Tween 80 were mixed in water to obtain a continuous phase (WP). 2 g of NIPAM, 0.04 g of BIS-AAm, 0.045 g of APS, 3 μL of TEMED, and 0.101 g of Tween 80 were dissolved in WP. Then 10 mL of a disperse phase containing kerosene (OP-1) was mixed using a homogenizer to obtain an emulsion for 2 min. Prior to polymerization, the stock solution was kept below 1℃ to prevent reaction. Another oil phase (OP-2) containing 80 mL of xylene and 1.42 g of Span 80 were prepared. Then OP-1/WP emulsion was mixed with OP-2 by a stirring blade to make a double emulsion in a three necks flask for 2 hours at 20℃ under nitrogen atmosphere. After the polymerization, microgels were purified by paper filter, followed by washing with isopropanol and distilled water. Afterwards, microgel suspensions were soaked in liquid nitrogen for several minitues and kept under reduced pressure to dry microgels.

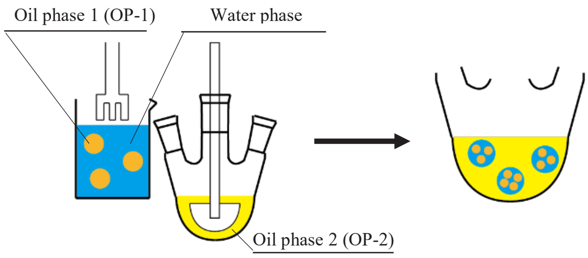

Fig. 1 Schematic illustration of making OP-1/WP/OP-2 emulsion.

3. Results

The size distribution of the microgels was evaluated by an optical microscope with a CCD camera at room temperature as shown in **Fig. 2(a)**. **Fig. 2(d)** shows the linear swelling ratio, d/d_{20}, obtained for the microgels. The particle diameter, *d*, as a function of the observation temperature was normalized by that at 20°C. The particle sizes were measured in a homemade cell. The temperature was varied in range 20℃ to 40℃. The d/d_{20}s for the heating and cooling processes clearly overlapped with each other, suggesting there was no hysteresis in these experimental conditions.

Subsequently, transmission ultrasound measurements were carried out using two water-immersion transducers. **Fig. 3 (a)** shows the attenuation coefficient α and the speed of sound, *c*, of PNIPAM-microgel suspensions as a function of frequency at 25℃, 28℃ and 32℃. **Fig. 3 (b)** shows the parameters by evaluated by the Faran's scattering

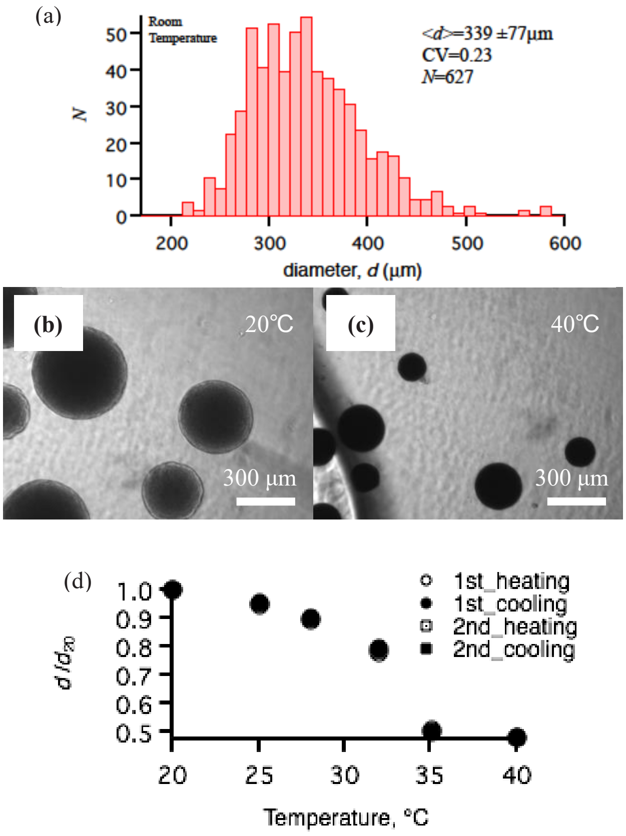

Fig. 2 (a) Particle size distribution obtained by an optical microscope at room temperature. (b,c) Optical micrographs of PNIAPM microgel in water at 20℃ and 40℃. (d) Temperature dependence of linear swelling ratio.

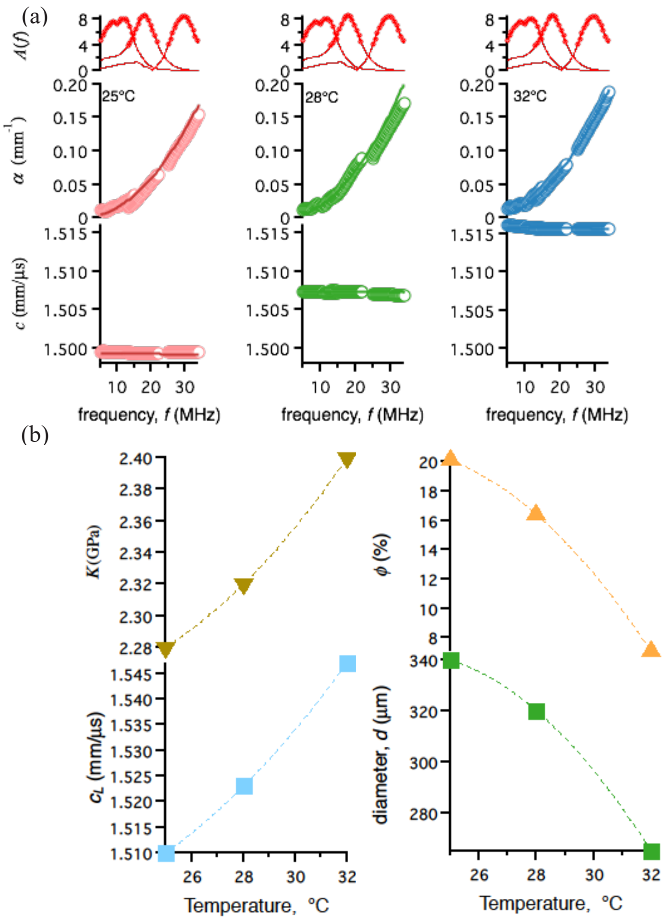

Fig. 3 (a) Transmission amplitude of ultrasound pulse as a function of frequency using 10, 20 and 30 MHz transducers and frequency dependences of α and c at 25℃, 28℃ and 32℃. (b) Temperature dependences of C (wt%), d and c_L by the Faran's theory prediction.

theory for microgel particles where d is the average particle size, and c_L, is the longitudinal velocity, K is the bulk modulus with $K=\rho c_L^2$, and C is the weight concentration of the microgels.[7) In this study, density, ρ and shear velocity, c_S were respectively fixed to be 1.002 g/cm^3 and 0 mm/μm because they are insensitive to the theoretical curves. It was found that the C and c_L have an dominant effect on α and c while d plays an important role only for α. The results seemed to be physically relevant for PNIPAM microgels which showed a volume phase transition upon temperature stimulation.

4. Conclusions

Suspensions of thermo-sensitive PNIPAM microgel were measured using ultrasound spectroscopy. The temperature dependence of the size, concentration and bulk modulus were evaluated by the Faran's scattering theory and seemed to be consistent with the optical microscope results, suggesting that ultrasound spectroscopy technique could be a potential tool to investigate thermo-sensitive microgels for drug release applications.

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