Structure analysis of acrylic emulsion particles and films by small-angle X-ray scattering

An aqueous polymer emulsion, a dispersion of water-insoluble polymer particles with diameters in the range of 50–500 nm stabilized by surfactants, is widely used for coatings and adhesives. The emulsion particles coalesce to form continuous films upon drying after application. It is important to clarify the particle structure and coalescence process that govern the film properties such as mechanical strength. We have characterized polymer dispersion liquids and films by small-angle X-ray scattering (SAXS) at SPring-8.

Three kinds of acrylic polymer emulsions with particles of various diameters at a glass transition temperature (Tg) of −70°C were prepared using surfactants with different structures (Table I). SAXS measurements were performed at beamline **BL08B2** with an X-ray wavelength of 0.15 nm and a camera length of 6050 mm. The size of the primary X-ray beam at the sample position was 0.5 × 0.5 mm^2. The coalescence process during drying of the emulsions at room temperature was monitored in terms of the emulsion concentration. Hydrodynamic particle sizes were also determined by dynamic light scattering (DLS) analysis using NICOMP™ 380 (Particle Sizing Systems).

Figure 1 shows SAXS profiles of a series of polymer emulsions during a drying process. The plateau appears at q = 0.02 nm^{-1} in 3.13 and 6.25 wt% dilute or semidilute systems, respectively. This is observed as a peak that shifts to higher q with increasing concentration, and finally reaches q = 0.048nm^{-1} for the film (dark gray broken line). This q region is attributed to the close packing structure of the particles. On the other hand, the peaks at around q = 0.079 nm^{-1} are caused by scattering from the particles themselves and shift negligibly (light-gray chain line). From these results, it is found that the film is formed only by mutual contact of the particles without a change in particle size.

Figure 2 shows the I•q^2 *vs* q plot of SAXS profiles of the emulsion films with different particle sizes. A value depicted on the curve is the ratio of the peak position for higher order peaks or shoulders to the highest peak (the first peak) position. If the ratio corresponds to $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}\ldots$ in the SAXS profiles, it means that the particles are packed in the hexagonal structure. All three polymer emulsion films show hexagonal close-packed structures because the ratios agree well with the sequence, though the scattering spectra observed for all the samples are broad.

The spherical emulsion particles are hexagonally packed because of the coalescence in films since Tg of the polymers is lower than room temperature.

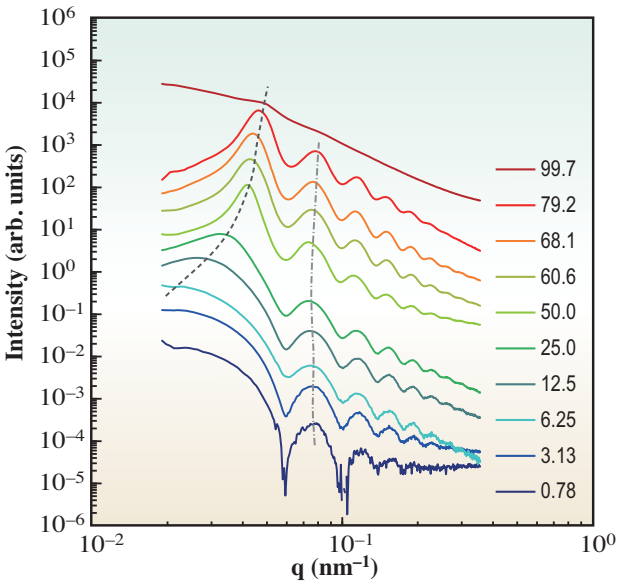


Fig. 1. SAXS profiles at various sample concentrations during dry process. Numerical values in the figure represent nonvolatile content in polymer emulsion. Dark gray broken line and light gray chain line represent the shift of the peaks upon close packing and the position of the peaks by scattering due to the particles themselves, respectively. Curves are vertically shifted.

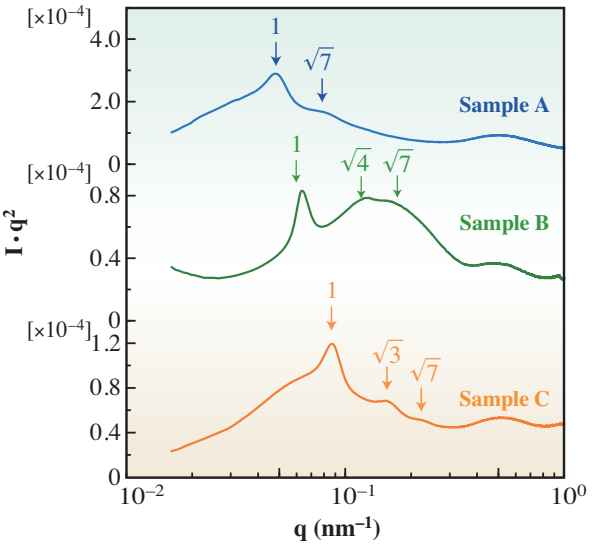
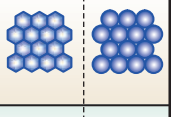


Fig. 2. I•q^2 *vs* q plot of emulsion films. Ratios of position of higher order peaks or shoulders to that of the 1st peak are also indicated.

Table 1. Diameters in emulsion films and solutions obtained from SAXS and DLS results, corona sizes, and the extended molecular lengths of the surfactants

	in solid		in solution			Corona size	Extended molecular length of surfactant
	Size of hexagonal particles	Size of sphere before coalescence estimated by eq. (1)	Diameter by SAXS	Expected diameter by SAXS	Diameter by DLS		
	(nm)	(nm)	(nm)	(nm)	(nm)	(nm)	(nm)
Illustrated structure / Sample code							
Sample A	130	143	153		174	10.6	9.86
Sample B	99	109	–	119	144	12.3	9.86
Sample C	72	80	–	90	111	10.6	7.72

The distance between the particles estimated from SAXS profiles corresponds to the size of the hexagon, (refer to the second column in Table 1). The diameter of the spherical particles before coalescence can be converted by $d = 0.74^{1/3} D$, where d and D are the size of the hexagon and the diameter of the spherical particles before coalescence, respectively. D is shown in the third column in Table 1.

The particle diameter of the 6.25 wt% sample is 153 nm, which is 10 nm larger than that in the film (solid). Because it is reported that poly(methyl methacrylate) has a swelling layer of 10-nm-thick in water [1], it is considered that the diameter of the particles in water becomes about 10 nm larger owing to swelling. Considering this phenomenon, it will be expected that the particle diameters for samples B and C in water may become 10 nm larger when determined from SAXS.

Volume-average diameters measured by DLS become large, as shown in Table 1. SAXS data gives the particle sizes from the difference in electron density between water and particles, whereas DLS yields the hydrodynamic sizes including the extent of surfactant in water. The extent of the surfactant in water, i.e., corona size, is calculated from the difference in sizes obtained from SAXS and DLS data and are listed in Table 1. The corona size for each sample is about 10 nm irrespective of the particle size.

Finally we calculated the extended molecular length of the surfactants for comparison with the corona size (Table 1). The lengths of the surfactants are found to be about 10 nm, and there is a reasonable agreement between the lengths and the corona sizes, being explained by the extension of the molecules in water owing to the repulsion between the ionic head groups of the anionic surfactants. Estimated emulsion particles are schematically shown in Fig. 3.

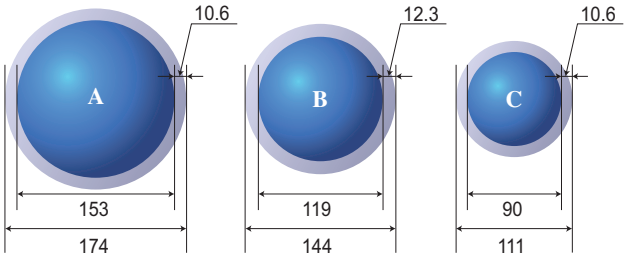


Fig. 3. Schematic models of the emulsion particles with various diameters. Deep and light blue areas indicate the sizes of the core and the corona of the emulsion particles, respectively.

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References

[1] K. Tanaka *et. al.*: Langmuir **24** (2008) 296.