

## AFM Observation of Growing Poly Isobutyl Methacrylate (PiBMA) Particles

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The growth process of poly(isobutyl methacrylate) (PiBMA) particle prepared in soap-free polymerization using V-50 as an initiator was observed by atomic force microscopy (AFM) to clarify the growth mechanism. As a result, it was found that PiBMA particles were capable of growing by the adhesion of smaller particles, which generated freshly during the particle growth period, to their surfaces.

Polymeric particles have been prepared by various methods. To control the size, size distribution, and surface property of the polymeric particles, it is very important to know the nucleation and growth mechanisms of the particles. Especially, the mechanism of soap-free polymerization of various monomers has been investigated intensively by many studies because this polymerization, where no emulsifier is employed, is simple but fundamental and the surface property of the particles is not contaminated by the additional stabilizers.<sup>1-3</sup> However, the process has not been necessarily clarified yet.

In our recent research,<sup>4</sup> the nucleation process of the particle in the soap-free polymerization using styrene was able to be observed in water with molecular scale using atomic force microscope to clarify the nucleation mechanism. Thus, we think the atomic force microscopy is very powerful tool to investigate the formation process of polymeric particles with molecular scale.

In this present study, it was reported that we observed growing poly(isobutyl methacrylate) (PiBMA) particles in the soap-free polymerization in water using AFM to derive the growth mechanism.

The soap-free polymerization of iBMA was performed in a round-bottom reactor of 500 mL with four-necks for stirring mechanically with a Teflon blade, condensing the reflux with the water, flowing nitrogen gas into the reactor, and sampling an aliquot of the solution with a pipet. Polymerization experiments were carried out as follows. Firstly, a given amount of distilled-deionized water from which the dissolved oxygen gas was removed by bubbling nitrogen gas was poured into the reactor under nitrogen atmosphere, and heated up to a given temperature by a water bath, agitating with the impeller of 185 rpm, and then the monomer isobutyl methacrylate (iBMA, Kanto Kagaku) was added. Finally, an aqueous solution of 2,2'-azobis(2-methylpropanamide) dihydrochloride (V-50, Wako Pure Chemical) was added to start the polymerization. Here, using V-50 as a cationic initiator makes all of polymerized products positively charged to adsorb negatively charged mica surface with molecular scale smoothness. All reagents were used without further purification. The recipe of the polymerization is shown in Table 1.

The particle size,  $D_p$ , of PiBMA particles was determined by averaging the data of ca. 200 particles from the images using a field emission scanning electron microscopy (FE-SEM, JSM-6340FS, JEOL). The SEM samples were prepared as follows:

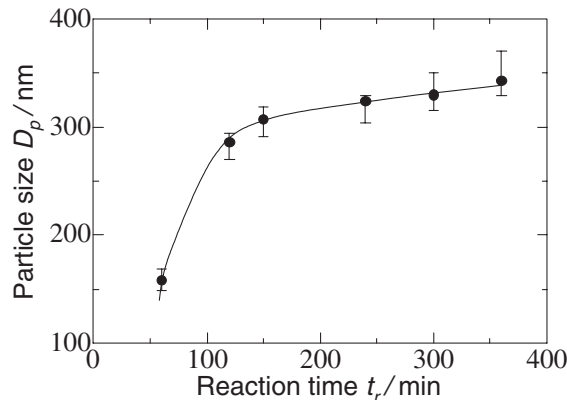
**Table 1.** Experimental Conditions of the Present Polymerization of iBMA

Water	iBMA	V-50 Solution	Reaction Temp.
120 g	6.5 mL	0.186 g/ 10 g-water	46 °C

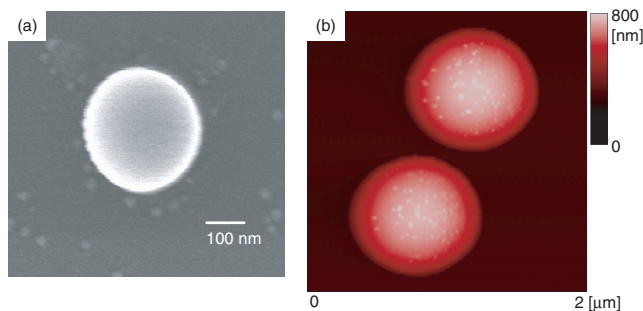
each small amount of solution was sampled from the reactor at given times, and then a drop of solution was placed on the freshly cleaved mica plate. Because particles were positively charged, they adsorbed easily on the mica surface of negatively charge. The excessive reactants in the drop were removed by rinsing with pure water. Then, the specimen was freeze-dried following the usual procedure and coated with a thin gold film by vapor deposition.

The atomic force microscope (Nanoscope III, Digital Instruments) was used to observe the PiBMA particles in water. Samples for AFM observations were prepared as follows. A drop of the solution was sampled from the reactor at a given time and then cast on the mica surface, such that particles were able to adsorb on the mica plate electrostatically. After the plate was set to the AFM liquid cell, pure water was injected into the cell to remove excessive materials and to terminate the reaction at the same time. AFM images of PiBMA particles adsorbed on the mica surface were obtained using the tapping-mode procedure with cantilevers whose spring constant were 0.58 N/m, where driving frequency of the cantilever was adjusted around the resonance frequency. All the AFM observations were carried out at room temperature of  $25 \pm 2$  °C.

Figure 1 shows the growth curve of PiBMA particle size measured by SEM to know how long the particles keep growing. It was confirmed that PiBMA particles continued to grow at least up to reaction time  $t_r = 360$  min. We tried to observe the growing PiBMA particles at  $t_r \leq 360$  min in detail using SEM and AFM to know the growth process.



**Figure 1.** Growth curve of PiBMA particle measured by SEM at the reaction temperature 46 °C.



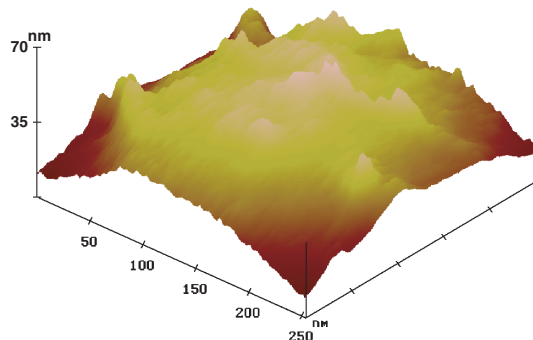
**Figure 2.** (a) SEM image of PiBMA particles at  $t_r = 240$  min. (b) AFM image of PiBMA particles at  $t_r = 240$  min.

At first, a SEM image of PiBMA particles at a reaction time  $t_r = 240$  min is shown in Figure 2a, where exists a large particle whose size is about 320 nm surrounded with many tiny particles. This indicates that the nucleation processes occur to generate new small particles in the existence of the growing particles. Generally, it has been thought that nucleation process and particle growth process are separated as LaMer's diagram shows.<sup>5</sup> Appreciating this SEM image, however, we thought that the nucleation occurred simultaneously besides the particle growth in the present system. It is possible to think that the present system has enough initiators and monomers to generate new particles in the bulk even at  $t_r = 240$  min.

We tried to clarify what were the contributions of these newborn small particles to the growth process of particle if any. About Figure 2a, because PiBMA particles in SEM images were covered with gold film for preparing, it was impossible to observe their real surface using SEM. If the surfaces were observed using AFM, we could observe the real surfaces with molecular scale. So, we tried to observe the surface of PiBMA particle at  $t_r = 240$  min in water using AFM.

Figure 2b shows an AFM image of the PiBMA particles at  $t_r = 240$  min in water using tapping-mode AFM. It was found that there were many smaller particles, as can also be seen in Figure 2a, adsorbed on the surfaces of PiBMA particles. This experimental result suggests that the existing PiBMA particles grow by the adhesion of newborn small particles, which generate during the particle growth period, to their surfaces. This suggestion is strongly supported by Figure 3, where a surface image of PiBMA particle at  $t_r = 330$  min in water using tapping-mode AFM are shown. The reason is that the surface had the roughness which would result from the adhesion of small particles.

If the existing particles can grow by the adhesion of newborn tiny particles, it can be predicted that decreasing initiator concentration will be able to prevent them from growing more because the number of tiny particles generated freshly during the particle growth period will decrease. So, we investigated



**Figure 3.** Surface image of PiBMA particle at  $t_r = 330$  min.

**Table 2.** Influence of initiator concentration on size of PiBMA particle

Initiator Concentration /mmol/L	0.88	5.27
Particle Size /nm	152	340

Water: 130 g, iBMA monomer: 6.5 mL, and reaction temp.: 46 °C.

the influence of the initiator concentration on the size of PiBMA particle, as shown in Table 2. It was clear that the particle size decreased as the initiator concentration decreased, as we expected on the basis of our experimental results.

By AFM observation of growing PiBMA particles prepared by the soap-free polymerization, the adhesion process, which is the adhesion of tiny particles generated freshly to the growing particle, was found in the growth process of PiBMA particle and it can explain why the size of final particles becomes larger as the concentration of initiator increases. Thus, this atomic force microscopy should be applicable to the clarification of the growth mechanisms of various polymeric particles. In the nearest future, we will discuss the earlier stage of the growth process.

## References

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