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Study of the Internal Structure of Latex Dispersions by Laser Scanning Microscope. Confirmation of Void Structure

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By using a confocal laser scanning microscope, the presence of stable, three-dimensional void structures in highly purified latex dispersions was confirmed.

The structural inhomogeneity in macroscopically homogeneous latex dispersions was first mentioned by Hachisu et al. by using a metallurgical microscope.[1] With the aid of such a microscope, Ise et al. also noticed the existence of non-space-filling, localized ordered structures of a high particle density together with disordered regions of low particle density (the two-state structure).[2] Macroscopically discernible, large-size ordered structures (or crystallites) in latex dispersions have been reported by other researchers.[3-5] Yoshiyama and Sogami[5] photographed large crystallites using Lang's method[6] and their crystal structures were precisely determined by Kossel line analysis. In their case, the photographs were taken after a latex dispersion were kept standing for about six months.

Another type of structural inhomogeneity in latex dispersion, namely voids, was first noted by Hachisu et al.[1] Later, micrographs of voids were reported by Ise et al.[7,8] and Kesavamoorthy et al.[9] Since these observations were made using a metallurgical microscope, and since only particles in the region near the dispersion-container glass interface (10 μm) can be observed in turbid dispersions, the question was raised whether this unanticipated structure was an artifact due to the so-called wall effect. In order to answer it, we employed a confocal laser scanning microscope (LSM) and have studied the internal structure of latex dispersions. In a previous paper,[10] we discussed the localized ordered structures and their growth. It was found that the inter-particle spacing in the ordered structure was in practice independent of the distance from the glass wall (up-to 50 μm) and the crystallization proceeded, layer by layer, from the region close to the glass interface to the region inside the dispersion. In this paper we report that three-dimensional (3D) void structures are real and argue that the artifactual factor can be ignored.

The styrene-based latex (N1000, diam.:0.96 μm, charge density:12.4 μC/cm^2) was supplied by Sekisui Chemical Company, Osaka. A laser scanning microscope (LSM:Carl Zeiss, Oberkochen, Germany) was used with an oil immersion objective of 100x with a 5 mW Ar laser. All experiments were carried out under density

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matching conditions using D_2O and H_2O. The LSM was not reversed type so that the upper part of the latex dispersions could be studied, while only the bottom or side part had been observed in previous measurements using Axiomat IAC. The temperature of the dispersions was kept constant by using a thermostated air bath.

As described in our previous paper,[11] the latex dispersions were extensively washed first using an Amicon Model 202 and Diaflo XM300 with Milli-Q reagent grade water. Then the dispersions were mixed with highly purified ion-exchange resins and allowed to stand or forced to rotate to attain quick ion exchange, until the resin particles started to "float" in the dispersions, indicating that three-dimensional ordering of latex particles had developed. After this stage, the dispersions were brought into an observation cell along with Bio-Rad ion-exchange beads [AG501-X8(D)], which had been washed with the freshly obtained Milli-Q water. The whole mixture was shaken vigorously, and was placed on the microscope bench. After shaking, the distribution of particles was confirmed to be homogeneous. After the dispersion had been left standing for 24 hours, void formation was observed. The void-containing dispersion was again shaken, homogeneous particle distribution was confirmed, and the dispersion was again allowed to stand for 24 hours on the microscope bench. Thereafter scanning micrographs (Fig. 1) were taken.

Figures 1-a and 1-b show that, while the dispersion was kept standing, the distribution of particles (white dots) clearly changed from "homogeneous" to "inhomogeneous". On the micrographs one can see particles and void structure at vertical distances of 10 and 20 μm from the top of a 3% dispersion under the density-matching condition. Note first that the void shown is as large as about 25 μm in diameter. Secondly, the cross section becomes larger with increasing distance from the top. Although not clear from Fig. 1, it has also been possible to observe void structures as long as 50 μm in the vertical dimension.

If the wall effect causes the void structure, its occurrence should be limited to the region near the wall. The increasing cross section at larger distances from the wall, as shown in Fig. 1, rules out the artifactual nature of the void formation. Another factor to be considered is adsorption of latex particles by coexisting ion-exchange resin particles. Even if the adsorption really happened, it should entail lowering of latex concentration in a homogeneous way throughout the dispersion volume, but not formation of voids in the localized manner.

Figure 1 shows the coexistence of the void structure and disordered particles. This is in a contrast with our previous results, in which ordered regions were found to coexist with void structures (Fig.2(A) of Ref. 12, Fig. 2(a) of Ref.13 and Fig. 8.1. of Ref.14). Further study is necessary to identify the factors controlling the coexistence of voids with ordered particles or with disordered ones.

It is almost impossible at present to make general statements on where the void can be formed, how large it may be and how long it can survive. The information on size given in the previous[8] and present papers has been confirmed but should not be taken as representative. Though the same thing can be said for the lifetime of the void, it would be worthwhile pointing out that voids were stable over the observation period (14 s), during which the focal plane of LSM was shifted from one depth of observation to the next. Note that this statement does not imply that the lifetime was as short as 14 s but the void was maintained for a minimum of 14 s.

Stable void structures really exist, though it is certainly astonishing in light of the homogeneous appearance of the dispersions. It should be emphasized that the void structures such as shown in Fig. 1 are too small to detect by naked-eye observation and too large to study by existing scattering methods.

We believe that the void structures provide direct evidence of the attractive interaction between latex particles, which we have claimed from previous experiments.[15] Because of this interaction, particles at the edge

of the void structure are able to remain at that location.

It is widely believed that colloidal systems can be described in terms of the repulsion-only assumption without considering attractive forces. As has been shown by several groups,[16-19] properties of the colloidal systems such as the structure factor, radial distribution function and shear modulus, can be equally satisfactorily described both by the widely accepted (purely repulsive) Yukawa (or DLVO) potential, and the Sogami potential containing short-range repulsion plus long-range attraction. The results mean that the applicability of the repulsion-only assumption is only superficial. While the true reason for this applicability seems to lie in the very shallow minimum of the interparticle potential, the void structure directly supports the idea of attraction: Further support comes from the re-entrant phase separation phenomenon of colloidal dispersions,[20] which can be described using the Sogami potential, but not by the Yukawa potential.

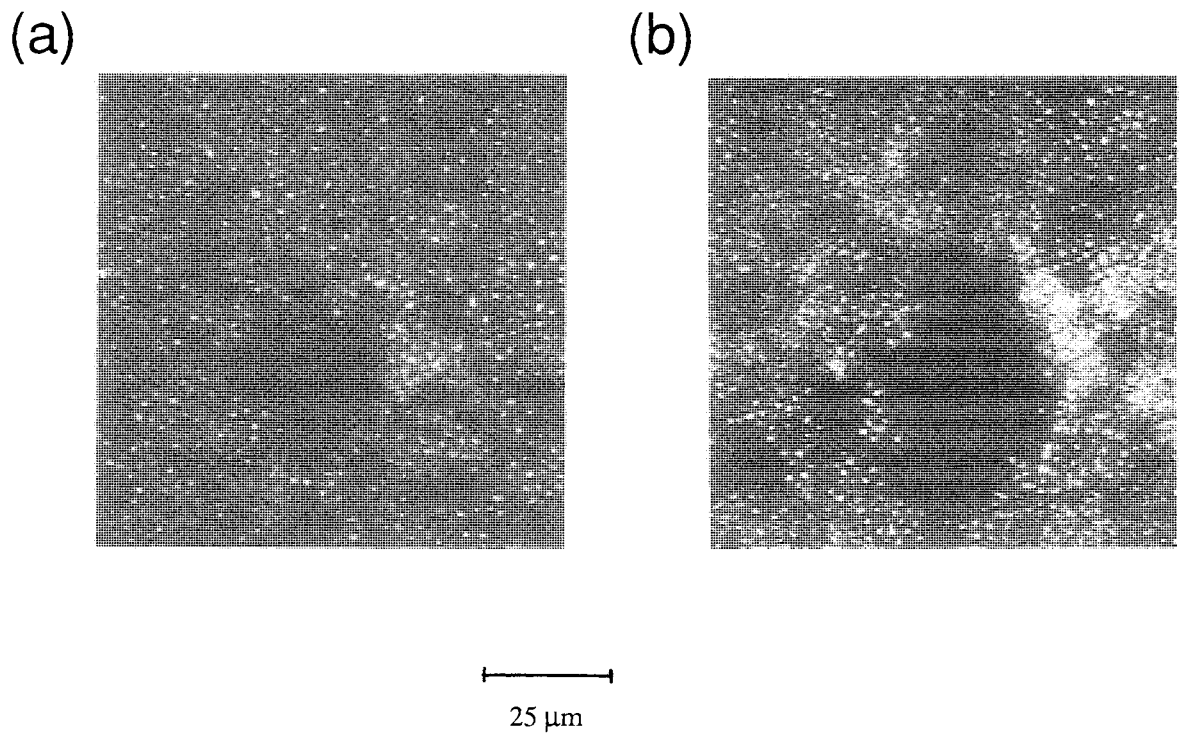

Fig.1. Void structure observed by a confocal laser scanning microscope. latex:N1000, concn.:3%, solvent:a H_2O - D_2O mixture. The micrographs (a) and (b) were taken at 10 and 20 μm from the top of the dispersion. See the text for detail.

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