

Assembly of Latex Particles by Using Emulsion Droplets. 3. Reverse (Water in Oil) System

O. D. Velev*[†] and K. Nagayama[‡]

Nagayama Protein Array Project, ERATO, JRDC,
5-9-1 Tokodai, Tsukuba, 300-26 Japan

Received July 10, 1996. In Final Form: December 23, 1996

1. Introduction

The development of methods for the fabrication of advanced colloid materials is important for both today's and future technologies. A number of different schemes for obtaining suspensions of colloid particles with defined size, structure, and properties have been proposed.^{1–4}

One general method of particular interest is the use of colloid-sized substrates and templates for fabricating complex particles.^{1,5,6} A wide variety of colloid systems and methods could be used for that purpose. Two of the simplest methods, which have already been utilized for a long time, are the heterocoagulation of particles of opposite charges^{7,8} and the production of core-shell latex microspheres.^{9,10} New types of particulate colloid materials have been obtained recently by using microemulsion droplets^{5,11} or vesicles.^{5,12} The use of emulsions as compartmentalized systems for the preparation of complex particles has however been restricted to a few cases,^{10,13} like the precipitation of submicrometer organic particles inside emulsion droplets.¹³

Recently, we proposed to use emulsion droplets as colloid-sized templates, which gather and assemble particles, suspended in the surrounding environment^{14,15} The

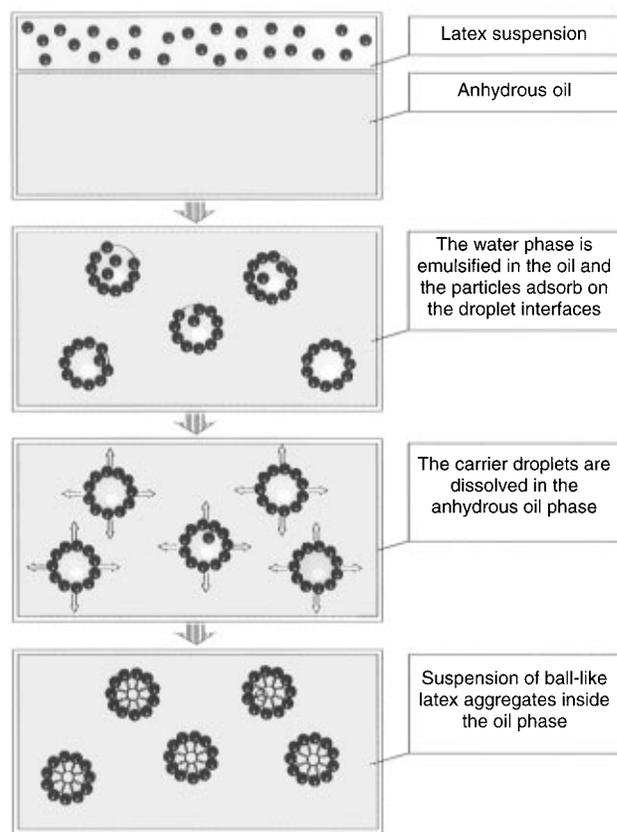


Figure 1. Basic scheme of the method for the preparation of spherical assemblies from latex particles by dispersing the aqueous suspension in anhydrous oil.

applicability of the method was demonstrated by using octanol droplets that assemble latex beads into bigger microstructural aggregates ("supraparticles"). After appropriate fixation (coagulation) of the supraparticle structures and their sterical protection, the carrier droplets are dissolved in the surrounding media. Multistep procedures were developed for obtaining suspensions of hollow,¹⁴ ball-like¹⁵ and composite¹⁵ supraparticles.

There appears to exist an even simpler method for the assembly of suspended colloid particles, by first dispersing their environment as emulsion droplets, each of which confines a number of particles. The assembly and extraction can then be performed by dissolving the droplets in the surrounding environment. In this note, we describe a simple method for the assembly of microspherical aggregates out of latex particles, confined in the droplets of a reverse, water-in-oil (W/O), emulsion.

2. Experimental Section

The polystyrene latex microsphere suspensions were supplied from IDC Co. (USA). All of the suspensions contained monodisperse particles of diameter close to 1 μm . A summary of the surface properties of the latexes is applied in the Supporting Information to the first paper of this series.¹⁴ The fluorescent latex contained a Texas Red dye. Prior to being used, the contents of the bottles were redispersed and sonicated for a few minutes. The suppliers and the quality of the chemical reagents are listed in the first paper.¹⁴

The emulsions of water in 1-octanol were dispersed with the use of a rotor/stator type homogenizer (Janke and Kunkel Ultra-Turrax T25, with a S-25N 10G dispersing tool). The emulsions and latex supraparticle dispersions were prepared in volumes of 3–5 mL, stored in tightly capped test tubes. During sample preparation and handling, inhalation of the irritating octanol fumes should be avoided.

* Author for correspondence: e-mail, velev@che.udel.edu.

[†] Present address: Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716.

[‡] Present address: Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153 Japan.

(1) Matijević, E. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 176.

(2) Fendler, J. H.; Meldrum, F. C. *Adv. Mater.* **1995**, *7*, 607.

(3) (a) Okubo, M. *Preprint of 3rd International Symposium on Radical Copolymers in Dispersed Media*, 1994, Lyon, p 68. (b) Matijević, E. *Chem. Mater.* **1993**, *5*, 412.

(4) Honda, H.; Koishi, M. In *Construction of Very Small Particles*; Koishi, M., Ed.; Kogyo Chosakai Publishing Co.: Tokyo, 1987; pp 127–203 (in Japanese).

(5) Fendler, J. H. *Membrane Mimetic Chemistry, Characterisations and Applications of Micelles, Microemulsions, Monolayers, Bilayers, Vesicles, Host-Guest Systems*; John Wiley Publishers: New York, 1982.

(6) (a) Mann, S. *Chem. Ind.* **1995** (3), 93. (b) Mann, S. *Nature* **1993**, *365*, 499.

(7) (a) Harding, R. D. *J. Colloid Interface Sci.* **1972**, *40*, 57. (b) Kawahashi, N.; Matijević, E. *J. Colloid Interface Sci.* **1990**, *138*, 534.

(8) (a) Furusawa, K.; Kizling, J.; Stenius, P.; Fendler, J. *J. Am. Chem. Soc.* **1983**, *105*, 2574. (b) Lopez-Quintela, M. A.; Rivas, J. *J. Colloid Interface Sci.* **1993**, *158*, 446. (c) Pileni, M. P. *J. Chem. Phys.* **1993**, *97*, 6971.

(9) (a) Okubo, M. *Macromol. Chem., Macromol. Symp.* **1990**, *35/36*, 307. (b) Winnik, M. A.; Zhao, C.-L.; Shaffer, O.; Shivers, R. R. *Langmuir* **1993**, *9*, 2053. (c) Dobler, F.; Affrossman, S.; Holl, Y. *Colloids Surf. A* **1994**, *89*, 23.

(10) (a) Otsubo, Y.; Kazuya, E. *J. Colloid Interface Sci.* **1994**, *168*, 230. (b) Walsh, D.; Mann, S. *Nature* **1995**, *377*, 320.

(11) (a) Kurihara, K.; Kizling, J.; Stenius, P.; Fendler, J. *J. Am. Chem. Soc.* **1983**, *105*, 2574. (b) Lopez-Quintela, M. A.; Rivas, J. *J. Colloid Interface Sci.* **1993**, *158*, 446. (c) Pileni, M. P. *J. Chem. Phys.* **1993**, *97*, 6971.

(12) (a) Mann, S.; Hannington, J. P. *J. Colloid Interface Sci.* **1987**, *122*, 326. (b) Yaacob, I. I.; Nunes, A. C.; Bose, A.; Shah, D. O. *J. Colloid Interface Sci.* **1994**, *168*, 289.

(13) Sjöström, B.; Bergenstahl, B.; Lindberg, M.; Rasmuson, A. C. *J. Dispersion Sci. Technol.* **1994**, *15*, 89.

(14) Velev, O. D.; Furusawa, K.; Nagayama, K. *Langmuir* **1996**, *12*, 2374.

(15) Velev, O. D.; Furusawa, K.; Nagayama, K. *Langmuir* **1996**, *12*, 2392.

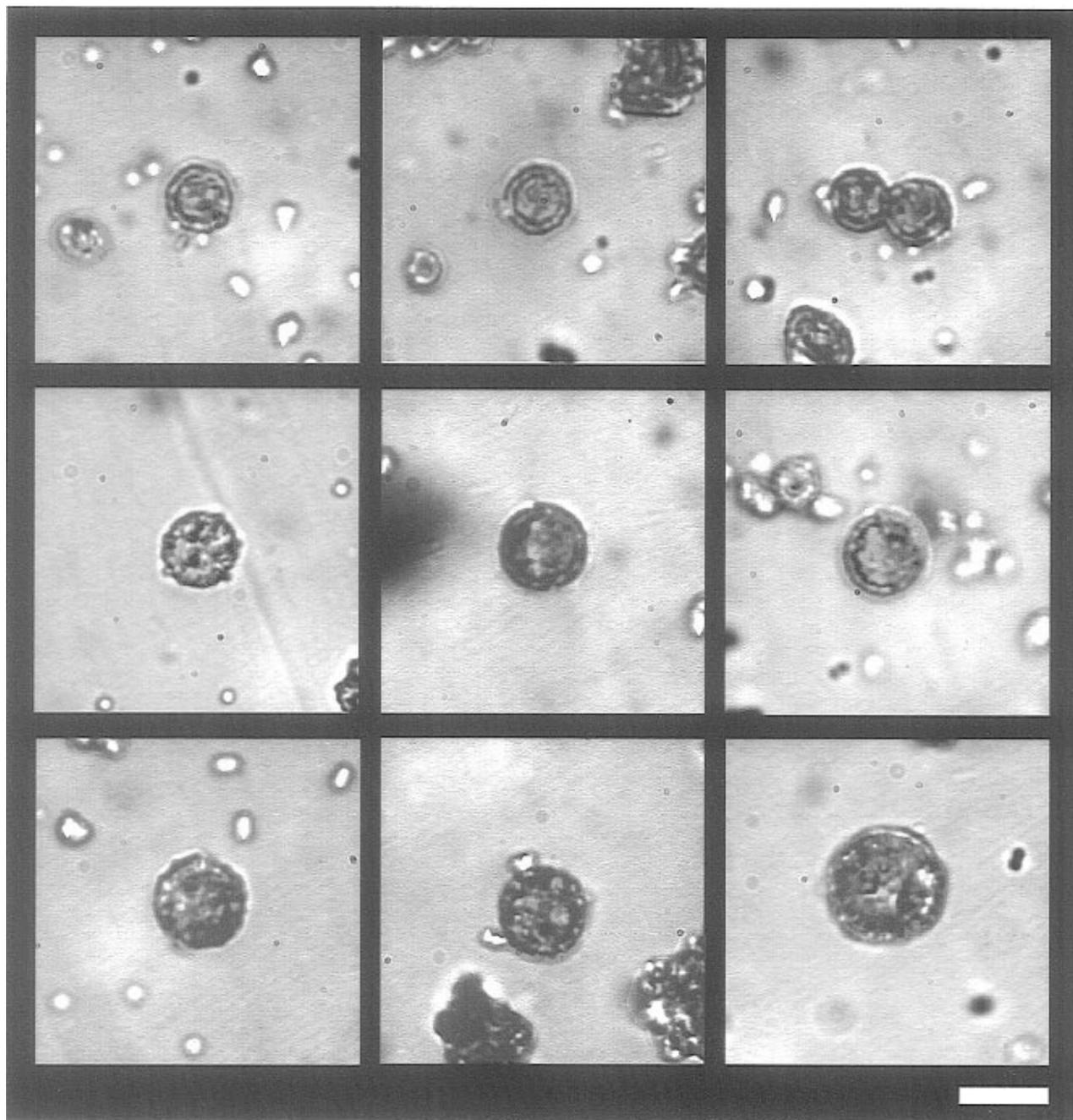


Figure 2. Digitized panel of microscopic pictures of the obtained spherical aggregates. To outline the polydispersity of the samples, droplets of various sizes are presented. White bar at bottom right = 10 μm .

The samples were observed by optical microscopy in transmitted or fluorescent (reflected) illumination. The microscopic equipment and procedures are described in the first paper of the series.¹⁴

3. Results

The basic scheme of the method is presented in Figure 1. The latex particles are initially suspended into the aqueous phase, which is emulsified inside the anhydrous octanol. A number of latex particles remain enclosed inside each droplet. These particles are adsorbed on the oil/water droplet interfaces, forming spherical shells. Subsequently, the water droplets inside the shells dissolve in the surrounding octanol environment, leaving behind the formed microscopic structures suspended in the oil.

To carry out the above scheme, a number of specific requirements should be implemented. First, the oil should

be able to dissolve the emulsified water phase completely and at an appropriate rate. Our preliminary experiments showed that the used octanol is able to dissolve up to about 6.5 vol % of emulsified water in a period of less than 5 min. A second requirement is the quick and strong adsorption of the latex particles on the droplet interfaces. The used sulfate latex in its original form was unable to adsorb promptly on the octanol/water interface. To induce adsorption, we modified the latex surface properties by using lysine monohydrochloride, as described in the previous paper.¹⁴

In the course of a typical experiment, the aqueous latex suspension was first mixed with lysine solution to obtain a final concentration of 6 wt % latex and 0.5 wt % lysine monohydrochloride. After 5–10 min, a small amount of the modified latex suspension was mixed with octanol. The system was homogenized for 2 min on the Ultra-

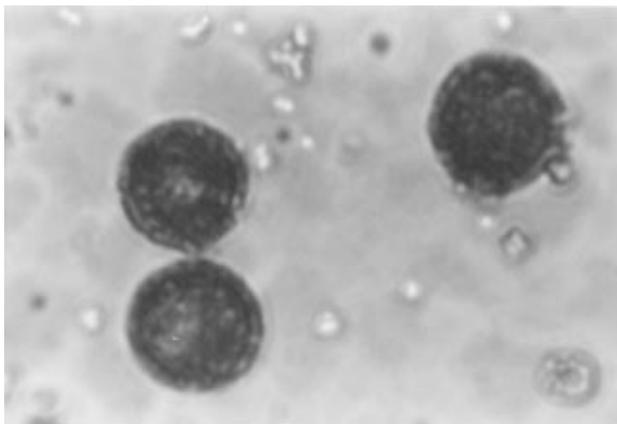


Figure 3. Microphotograph of a few supraparticles with low polydispersity within a single sample. The outer diameter of the spherical assemblies is 10–12 μm (cf. with Figure 2).

Turrax device at 8000 min^{-1} (rpm) and left for 2 min more at rest, before samples for microscopy were taken.

It was seen by microscopy that the final product of the process was spherical assemblies from aggregated latex with cavities in the center (these cavities usually contain a small amount of unadsorbed latex). In Figure 2, we present a variety of particles observed within two experimental runs with an initial water concentration of 6 vol % (see below). Particles of all possible sizes were selected to demonstrate the degree of polydispersity of the obtained assemblies. This polydispersity appears to be lower than in the case of O/W emulsion assembly schemes—compare with Figures 5 and 9 from the first paper.¹⁴ Very similar in size microspherical aggregates could be observed in some of the samples—Figure 3. The observation of the lateral ordering of the beads forming the shells was difficult due to the optical characteristics of the system. Ordered patches of particles in the shells could be noticed, but it did not appear that long-range order of all of the particles is present.

The obtained spherical assemblies were checked for absence of water by two independent procedures. First, the microspherical aggregates were cross sectioned optically by changing the focal position of the objective, as described in the first paper of this series. The absence of any droplets inside the latex shells was revealed by observation of cracked or incomplete particles (Figure 6 from ref 14). Second, we found out that the octanol is a strong quencher of the fluorescent ability of the Texas red colored latex and the fluorescence disappears after the beads become completely surrounded by octanol. This method was applied by using a mixture of common latex with 15% of fluorescent one. The dissolution of the water droplets was detected by the disappearance of any fluorescent flickers in the sample when viewed in fluorescence mode.

By using the above techniques we prepared and observed samples that contained initially 1.6, 6.0, and 6.6 vol % of latex suspension. In correlation with the preliminary octanol/water tests, no residual water was observed in the first two samples, after the homogenization/dissolution process. Small water droplets and fluorescence were detected in the third sample. There were significant differences in the quality of the obtained assemblies within the three samples. Only the second sample revealed a good yield ($\geq 50\%$) of original latex converted into closed spherical clusters. The sample with low initial suspension concentration showed a low yield of irregularly shaped clusters. This possibly resulted from the too quick dissolution of the template water droplets that does not

allow the formation of good quality ordered latex shells. In the third sample (6.6 vol %), some of the water droplets remained undissolved, and the quality of the obtained structures was very poor, due to droplet recoalescence and latex restructuring.

Our conclusion is that the dissolution of the droplets should be slow but complete, in order to obtain a good yield of spherical latex assemblies (Figures 2 and 3). To check this, additional experiments were carried out in a two-step scheme—first dissolving 2.5 vol % of water in the unsaturated octanol phase, and then dispersing the latex, suspended in another 2% of water. In this way we managed to obtain supraparticles of good spherical shape and with improved degree of lateral ordering of the particles. Thus the speed of dissolution turns out to be a major factor for controlling the process.

4. Discussion and Concluding Remarks

The scheme described above ends up with a suspension of microspherical latex aggregates in oil. The lower polydispersity of these microspheres in comparison to the ones obtained earlier in water environment possibly results from a shift of the homogenizer hydrodynamic action from turbulent to laminar,¹⁶ due to the higher viscosity of the octanol phase ($\eta = 10.6$ cP) in comparison to water. The volume part of the dispersed water phase in our experiments was restricted to a few percent, because of the limited solubility of water in octanol. This solubility, as well as the viscosity and other properties of the oil environment, could be in principle controlled by adding to the system a third component like ethyl alcohol.

It is appropriate to consider the mechanism of formation of the obtained microspherical aggregates. The latex particles in the original aqueous suspension are protected from coagulation by the charged sulfate groups on their surfaces that invoke repulsive electrostatic and hydration forces.^{17,18} To induce adsorption of these latexes on the oil/water interface, the magnitude of their surface charge needs to be reduced. This has been done by introducing lysine monohydrochloride (a mild coagulant) in the water droplets. As shown previously¹⁴ the lysine ions partially neutralize the negative charges of the particles to a degree when the latexes become hydrophobic enough to be adsorbed on the oil/water interface, but without lateral coagulation. This leads to the formation of the closed shells around the droplets. When the carrier droplets are dissolved in the oil environment, the particles in the shells are coagulated due to the attractive van der Waals forces and the absence of repulsive electrostatic repulsion in the oil. It is possible that the mechanical stability of the microclusters is also increased by lysine residues, deposited around and between the latex particles.

The obtained spherical assemblies were not protected against coagulation with each other by any repulsive interaction. For kinetic reasons, however, they remained suspended inside the viscous octanol phase for a period of a few hours, before sedimenting on the bottom. Once the microspheres settled down, they stuck together, because of the van der Waals attraction. As shown in the earlier papers, this can be avoided by introducing appropriate sterical protectors in the environment after the assembly.

In comparison with the methods for “supraparticle” assembly, described in the first two papers, the reverse

(16) Walstra, P. In *Encyclopedia of Emulsion Technology*; Becher, P., Ed.; Marcel Dekker: New York, 1982; Vol. 1, pp 83–102.

(17) Seaman, G. V. F.; Goodwin, J. W. *Am. Clin. Prod. Rev.* **1986**, June, 31.

(18) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1992.

emulsion scheme appears to be more simple and straightforward. As such, it can find application in industrial processes, where the assembly of small colloid clusters suspended in oil phase is required. On the other hand, the range of its application is restricted by the use of reverse emulsions and specific oil phases. The complementary methods described in this note and the preceding papers could be used for the practicable production of novel colloid materials. The knowledge and multistep utiliza-

tion of a number of different colloid interactions are a prerequisite for the successful application of these methods.

Acknowledgment. The authors are thankful to H. Yoshimura and S. Ebina for their kind help and advice.

LA960652U