Colloid Polym Sci (1995) 273:76–82
© Steinkopff-Verlag 1995

ORIGINAL CONTRIBUTION

J. Lee
M. Senna

Preparation of monodispersed polystyrene microspheres uniformly coated by magnetite via heterogeneous polymerization

Received: 23 February 1994
Accepted: 12 May 1994

Prof. M. Senna (✉) · J. Lee
Keio University
Department of Applied Chemistry
Faculty of Science and Technology
3-14-1 Hiyoshi, Kohoku-kuu
Yokohama 223, Japan

Abstract Composite microspheres of core-shell type were prepared by a seeded polymerization using monodispersed polystyrene seed latex (Ps) combined with an in situ dispersion of magnetite (Fe_3O_4) fine particles. The heterogeneous polymerization was carried out in aqueous dispersions of the Fe_3O_4 particles modified with sodium oleate. All the synthetic processes were carried out in a wet state to avoid serious agglomeration. The morphology of the composite particle and the size distribution were examined to discuss the effects on the polymerization parameters, such as monomer concentration, type and concentration of an initiator, magnetite particle concentration and the method of surface modification of Fe_3O_4.

Key words seeded polymerization – magnetite fine particles – polymer microspheres – heterogeneous polymerization – surface modification

Introduction

Inorganic particles possess various functions such as high electrical conductivity, ferroelectricity or ferromagnetic properties, which are not imparted to organic polymers themselves. Many attempts were made to prepare composite particles with polymer core and an inorganic shell for the purpose of designing functional polymers [1, 2]. Those composite particles are expected to be used as a toner for xerography or laser printer, dry paints, drug delivery aids, medical diagnostic tests, and many other areas.

Preparation of uniform composite microspheres coated with inorganic fine particles can be accomplished by mechanical and chemical methods. Mechanical methods using such as a high-speed-stirred mixer or a high-shear mill are used for the preparation of microspheres containing functional particles [3]. Although the mechanical route is easy and convenient, this cannot always produce composite particles of high quality, partly due to uneven distribution of mechanical energy. Too weak mechanical energy causes poor dispersion of the particles, while excessive energy causes the particles to be buried in the core particle [4]. Crystallographical degradation of functional guest particles is another hazardous problem due to a mechanical method. Meanwhile, suspension polymerization under a dispersion of inorganic particles is used as a chemical method [2, 5, 6]. However, the composite particles produced by those methods have disadvantage of having a wide size distribution.

Monodispersed microspheres with their diameter in the range of a few micrometers were conveniently prepared by a dispersion polymerization. Surface, and bulk properties of such monodispersed microspheres can be modified by a subsequent seeded copolymerization, e.g., of styrene and divinylbenzene in the presence of monodisperse polystyrene seed particles [7–9]. When a seeded polymerization coupled with the inorganic dispersion follows the dispersion polymerization, formation of the uniform composite microspheres is expected.

In preparing composite microspheres via a chemical route, surface properties of the inorganic particles, especially the affinity at an inorganic/polymeric interface, are of vital importance for the stable dispersion of the particles in the polymerization system, and hence the morphology control. Therefore, surface modification has almost always to be done for the preparation of composite particles.

In order to enhance the dispersibility of organic particles in an aqueous medium, coupling agents or surfactants are used [10, 11]. As the surface of metal oxide particles is generally covered by a number of OH groups in an aqueous medium, modification could best be done by the reaction of the surface OH and the vinyl group of coupling agents when the affinity to vinyl compounds is necessary [9]. Thus, we used seeded polymerization to obtain monodispersed composite microspheres of polystyrene and magnetite particles. To seek an appropriate surface modification of the guest Fe_3O_4 is also an important aim of the present study.

Experimental details

The materials

Styrene monomer was purified by washing with a dilute NaOH aqueous solution and distilled under reduced pressure. Monodispersed polystyrene seed particles in a single micron regime were produced by dispersion polymerization of styrene monomer using benzoyl peroxide (BPO) as an initiator and poly acrylic acid (PAA) as a stabilizer [12]. Magnetite was precipitated from a mixture of ferric chloride ($FeCl_3 \cdot 6H_2O$) and ferrous chloride hydrate ($FeCl_2 \cdot 3H_2O$), dissolved in distilled water in the molar ratio, 1 to 2. This mixed solution was added slowly into a 3.3 N NaOH aqueous solution at 80 °C while stirring at 400 rpm. The mixture was subsequently aged at 80 °C for 30 min. The suspension was cooled to room temperature and decanted. The magnetite was dialyzed for 1 week. All the synthetic processes were carried out in a wet state in order to prevent from agglomeration of particles during drying.

Surface modification of magnetite particles

Sodium oleate ($C_{17}H_{33}COONa$) was used for modification of magnetite particles. Sodium oleate (30 wt % with respect to Fe_3O_4) was added to the suspension of Fe_3O_4 and then ball-milled with 400 pieces of 16 mm glass balls for 24 h. For the purpose of characterization, the suspension of Fe_3O_4 was dried under reduced pressure (1.01×10^5 Pa). The dried Fe_3O_4 particles were characterized by the infrared spectra, to confirm the sodium oleate adsorption. The dispersibility in water was evaluated from the apparent particle size measured by a centrifugal automatic particle analyzer (CAPA-500, Horiba).

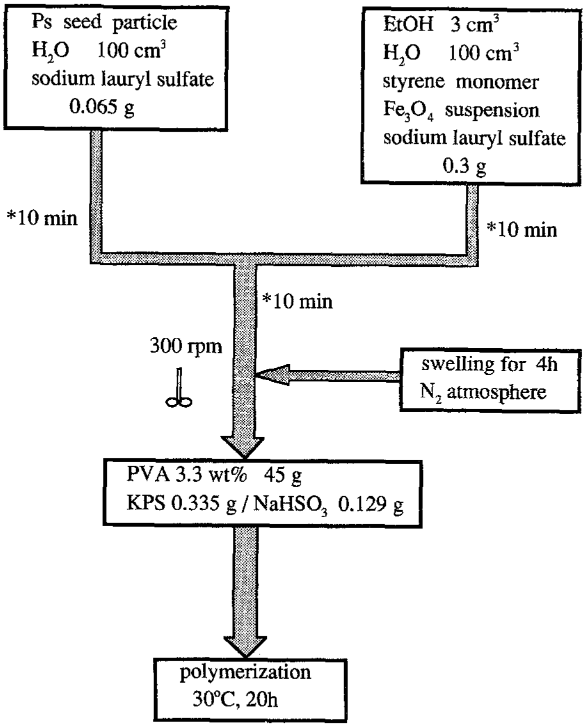
Zeta-potential of the Fe_3O_4 particles before and after modification was measured in a 10 mM NaOH buffer solution. Control of pH was made by adding HCl or NH_4OH solution. The Fe_3O_4 particles were also observed under the transmission electron microscope (TEM).

Preparation of composite particles

The scheme of the preparation of Fe_3O_4-polystyrene composite particles is shown in Fig. 1. The seed polystyrene latices were dispersed in 100 cm^3 ion exchanged water containing 0.065 g sodium lauryl sulfate.

A monomer emulsion was made from 3 cm^3 ethanol, 0.3 g sodium lauryl sulfate, styrene monomer of various concentration and 100 cm^3 ion exchanged water. Fe_3O_4 suspension was mixed with the monomer emulsion under ultrasonication for 10 min. Two solutions containing the latices and the monomer, respectively, were then mixed. The weight ratio of monomer/Fe_3O_4 are from 5/0.5 (g) to

Fig. 1 Schematic representation of the seeded polymerization



*dispersed under ultrasonication

20/2 (g). The quantity of seed particles was kept constant at 1 g. Swelling of polystyrene latices with styrene monomer was performed at 30 °C under gentle stirring at 300 rpm for 4 h. The initiator ($K_2S_2O_8$), was dissolved in an aqueous solution of polyvinylalcohol (PVA, 3.3 wt %) and added to the mixed solution. Polymerization reaction was carried out in a 500 cm^3 separable flask under N_2 atmosphere in a water bath at 30 °C for 24 h. The products were washed three times each with ethanol and ion exchanged water.

The composite particles were observed by transmission and scanning electron microscopes (TEM, SEM). Size distribution of the composite particles were obtained by a laser particle size analyzer (Malvern, Mastersizer S2.01).

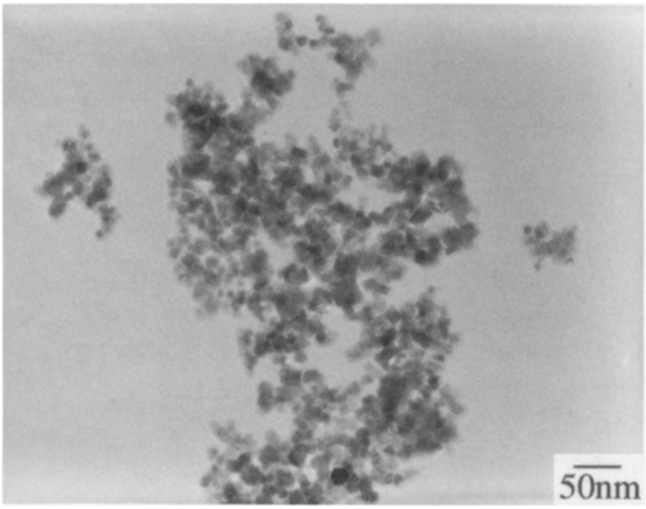
Results

Surface properties of magnetite

The average particle size of modified Fe_3O_4 particles was 10 ± 1 nm, determined by measuring more than 100 particles on the TEM photograph (see Fig. 2). Figure 3 shows IR spectrum of the Fe_3O_4 particles modified by sodium oleate. The absorption bands $2900 \sim 2850\ cm^{-1}$, $1470\ cm^{-1}$ and $1610 \sim 1550\ cm^{-1}$, $1400\ cm^{-1}$ were assigned to $-CH_2-$ and $-COO-$ of the sodium oleate, respectively.

The ζ-potential provides the information about the surface modification of Fe_3O_4 by the sodium oleate adsorbed on the surface of the Fe_3O_4 particles. The pH effect on ζ-potential is shown in Fig. 4. The isoelectric points (i.e.p) of Fe_3O_4 particles before and after surface modification by sodium oleate were 8.5 and 10, respectively. The dependence of ζ-potential on pH changed significantly by surface modification. It seems as if two curves were mirror images with respect to the horizontal line ζ-potential = 0. The ζ-potential at pH higher than i.e.p of the Fe_3O_4 became positive and that of the modified Fe_3O_4 became negative. The change in ζ-potential seems to be attributed to following factors. It was proposed by Meguro and Esumi that Fe_3O_4 particles have double adsorption layer when the surfactant concentration is above the critical micelle concentration (CMC) [13]. The first monolayer is due to the electric attraction between the positive surface of Fe_3O_4 particles and the anion of the surfactant. The outer layer is

Fig. 2 TEM photograph of Fe_3O_4 particles after modification



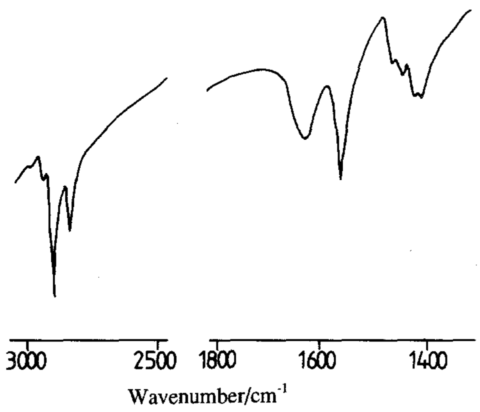


Fig. 3 IR spectrum of the dried Fe_3O_4 particles after modification

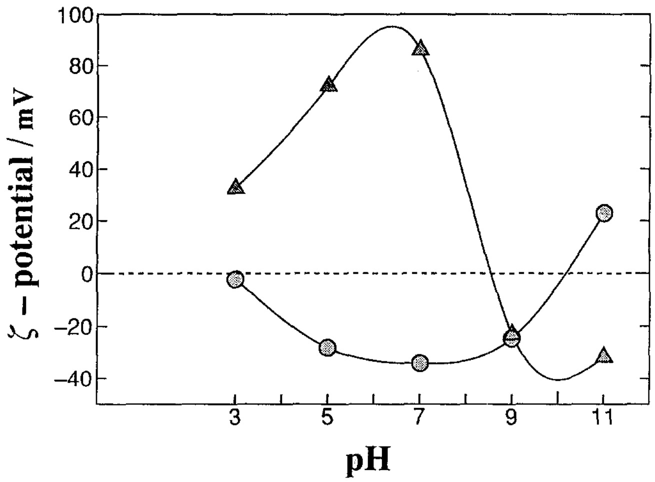


Fig. 4 The pH effect on ζ-potential of Fe_3O_4 particles before and after modification; before (△) and after (○) modification of Fe_3O_4 particles by sodium oleate

Table 1. Apparant particle size of Fe_3O_4 particles before and after modification measured by CAPA in different solvents.

	Styrene monomer (nm)	Aqueous solution (nm)
modified Fe_3O_4	1330	120
unmodified Fe_3O_4	850	900

composed of the physically adsorbed carbon-chain between sodium oleate molecules on the Fe_3O_4 particles and those in bulk aqueous phase. The Fe_3O_4 particles surface are recharged, since the anion of the adsorbed surfactant is oriented toward the aqueous phase. Fe_3O_4 particles are thereby dispersed stably by electric repulsion with each other.

These were confirmed by the apparent particle size in the aqueous medium shown in Table 1. It is generally observed that the apparent size of the particles decreases as the affinity between the particles and medium increases. The apparent particle size of Fe_3O_4 particles in the aqueous phase before and after modification was 900 nm and 120 nm, respectively at pH 5.38. The decrease in the apparent particles size seems to indicate an increase in the affinity between Fe_3O_4 particles and the aqueous solution. Modified particles were also dispersed stably in water at pH 5.38. On the other hand, in the styrene monomer the particles were agglomerated to give larger the apparent particle size since the surface of the particles did not have enough affinity for organic solvent. The apparent particle size of the modified Fe_3O_4 particles, 120 nm is much larger than the average primary particle size 10 nm, so that it is evident that Fe_3O_4 particles are still significantly agglomerated.

Morphology of composite particles

Figure 5 shows the morphology of composite microspheres. Micrographs revealed that the composite particle has a rough surface due to agglomeration of Fe_3O_4 particles. The composite particles were not dispersed in a unit of primary particles but agglomerated. As the weight ratio of Ps/Fe_3O_4 particles increased to 1/2, Fe_3O_4 particles were agglomerated more significantly. An increase in the extent of agglomeration of the composite particles is attributed partly to the increasing total free-energy of the surface due to the increase of the specific surface area of the ferromagnetic fine Fe_3O_4 particle and to the magnetic attraction. For these reasons, the present composite system has a tendency to agglomerate particularly due to the presence of Fe_3O_4 at the surface in order to stabilize itself.

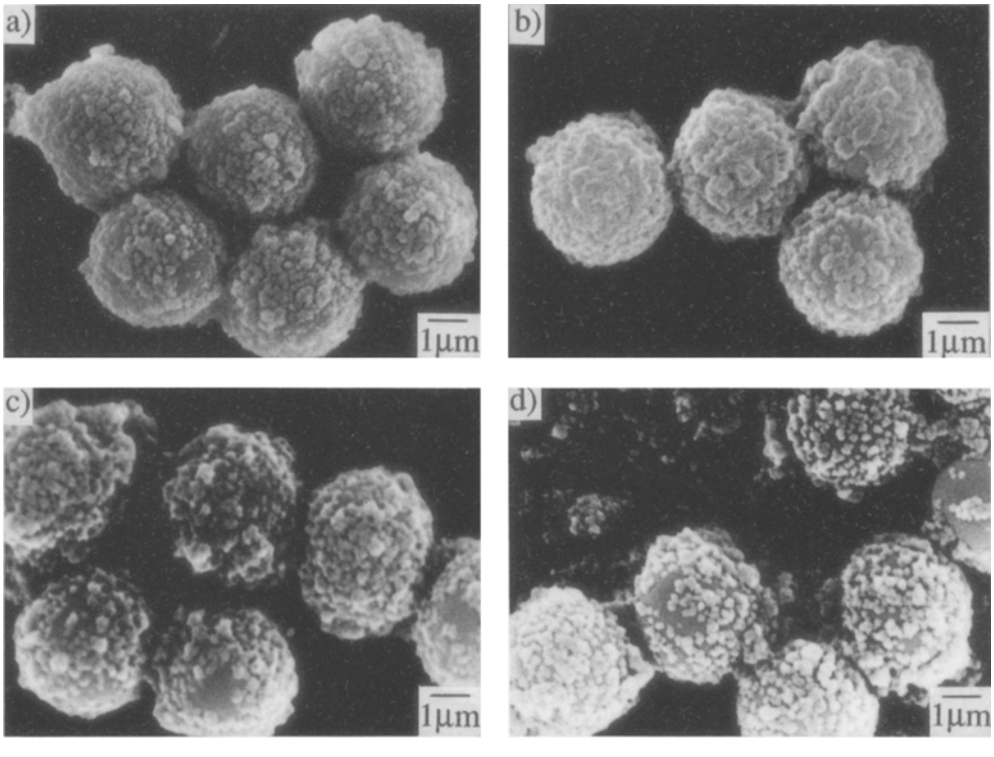


Fig. 5 SEM photographs of composite microspheres; (a), (b), the weight ratios of Fe_3O_4/monomer were 0.5/5, 0.5/20 and (c), (d), were 0.5/10, 2/10, respectively

Particle size distribution of the composites

The diameter of composite particle is expected to be above 3.5 μm, since an average particle diameter of the seed Ps was 2.95 μm and that of small composite particle adhere to Ps was about 0.3 μm. The average particles size of Ps and composite particles were determined by measuring more than 100 particles on the SEM photograph. Particle size distribution of composite particles was measured by laser particle size analyzer. The measured peak of the size distribution curve of composite particles, 4 μm, shown in Fig. 6, agreed fairly well with the expected size. Particles larger than 6 μm were due to agglomeration of composite particle. As the weight ratio of Ps/monomer increased from 1/5 to 1/20, the average particle diameter scarcely changed, but when the weight ratio of Ps/monomer was 1/15, the distribution became broad (see Fig. 6-a). The reason for this broadening is not clear at present.

Fig. 6 Size distributions of the composite particles; a) monomer increased from 5 g (M5) to 20 g (M20) with respected to Fe_3O_4 0.5 g, b) Fe_3O_4 increased from 0.5 g (F0.5) to 2.0 g (F2.0) with respected to monomer 10 g

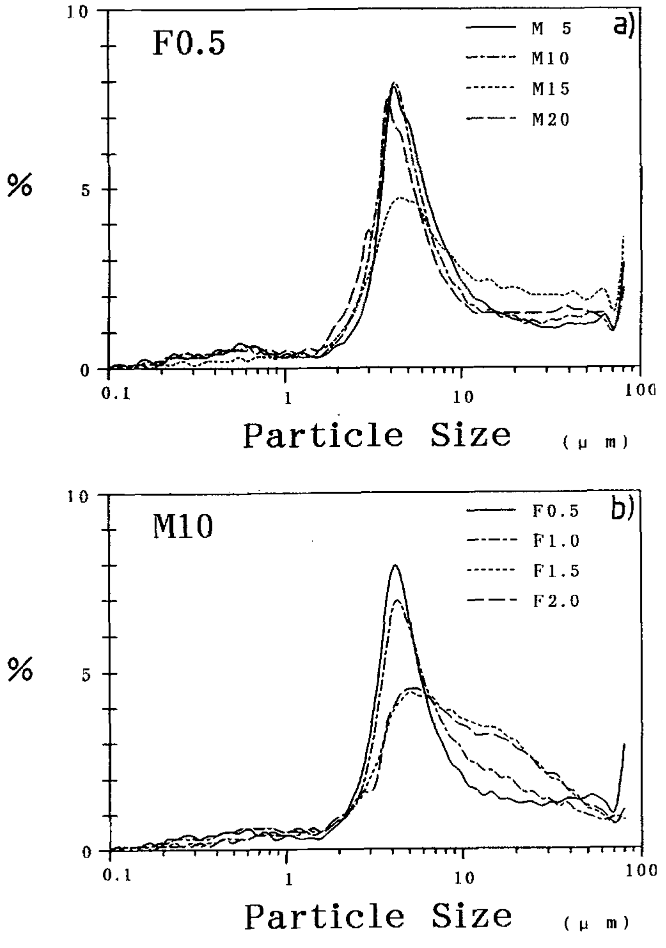


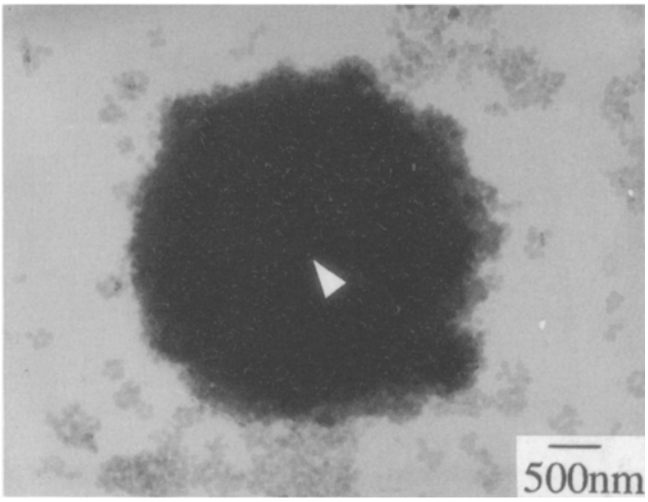
Figure 6-b shows the effects of Fe_3O_4 concentration on the particle size distribution. As the Fe_3O_4 concentration increased, the size distribution above 6 μm became broader. It seems that an increase of Fe_3O_4 concentration promotes a larger number of nucleation, and the particles produce agglomerates due to the magnetic attraction of the Fe_3O_4 particles.

Microstructure of the composite particles

TEM micrographs in Fig. 7 show that the composite particles consist of two kinds of particles. The smaller composite particles of about 0.3 μm in Fig. 8 are coated with Fe_3O_4 particles. The larger particle in the central part of Fig. 7 is the seed particle (Ps) covered with a number of smaller composite particles. The smaller composite particles were produced by emulsion polymerization, during which the monomer-swollen micelle was polymerized by the water-soluble initiator ($K_2S_2O_8$).

The cross-sections of the prepared composite particle are shown in Fig. 9. The bright areas of the microsphere in the figure represent Ps, and the outermost dark areas represent smaller composite particles. It is obvious that the composite particle of core-shell type was produced by emulsion polymerization of styrene monomer in the presence of polystyrene (Ps) seeds and fine magnetite particles. In order to estimate the strength of Fe_3O_4 attachment in the composite particle, washing was carried out for forced detachment. Fe_3O_4 did not detach even after vigorous washing, which suggests that the adhesion of Fe_3O_4 par-

Fig. 7 TEM photograph of composite particles, M20-F0.5: the larger particle of central part is Ps (see arrow) covered with a number of smaller composite particles



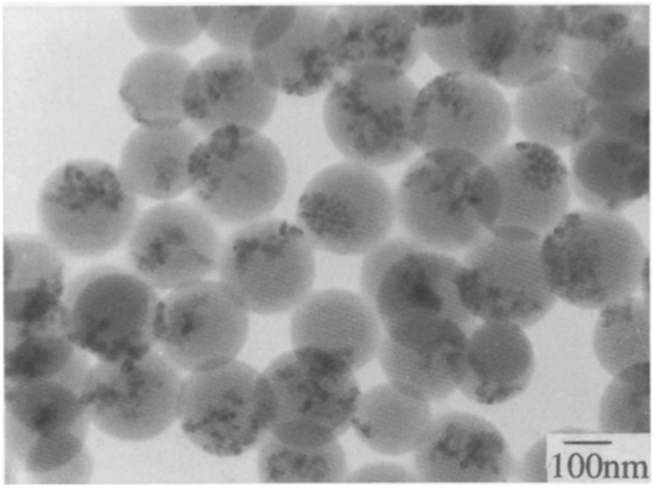


Fig. 8 TEM photographs of small composite particles M20-F0.5 coated with Fe_3O_4 particles

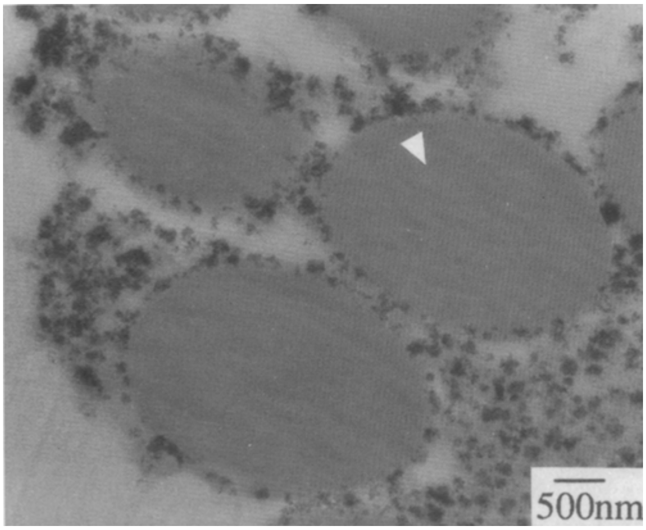


Fig. 9 Cross-section of composite microsphere M15-F1; the gray areas represent Ps (see arrow), and the outermost dark areas represent smaller composite particles

ticles is strong enough to endure conventional ultrasonication.

Discussion

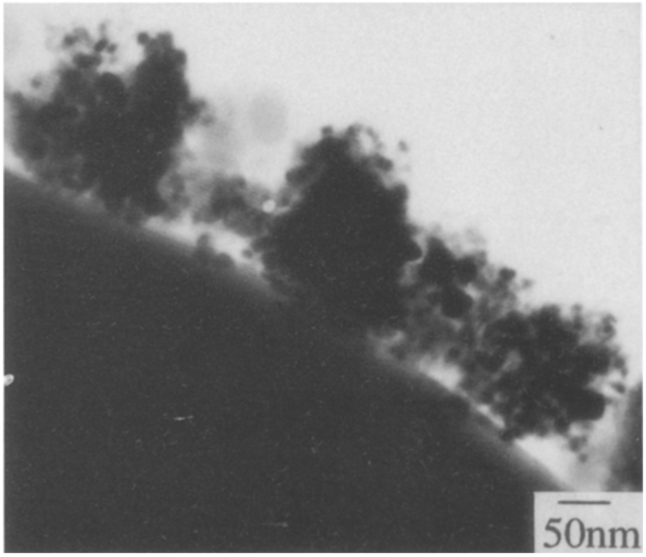
Seeded polymerization in the presence of seed particles is particularly useful for the preparation of large monodisperse polymer microspheres. Depending on the polymerization condition, however, formation of new particles takes place in the polymerization medium by emulsion polymerization [14]. Emulsion polymerization differs from dispersion polymerization in several important aspects, including the use of surfactant in the former instead of a polymeric steric stabilizer in the latter. While the multiple phases exist at the beginning of the emulsion polymerization, there is only one phase present in the reactant of dispersion polymerization [15].

In the present polymerization process, the surfactant, sodium lauryl sulfate, for seeded polymerization, seems to have stabilized the initial monomer emulsion. When water is used as the dispersing medium, micelles of the surfactant are formed which entrap the monomer molecules. According to Smith–Ewart theory [16], free radicals produced in the aqueous phase by decomposition of the initiator enter into micelles swollen with monomer. Monomer molecules were either captured in micelles or seed particles, or converted to oligomeric radicals after having added monomer molecules from their dissolved state [17, 18].

Polymerization is propagated in the micelles, monomer being supplied to them by diffusion from the aqueous phase. During polymerization with addition of seeds, a large number of new particles is formed when the emulsifier concentration is in the region of the CMC [19].

Since the water-soluble initiator was used, emulsion polymerization of styrene monomer may occur preferentially, instead of seed polystyrene swollen with monomer. The polymerization begins in the micelles of the emulsifier and continues in polymer-monomer particles formed from these micelles, in which further polymerization takes place.

Fig. 10 TEM photograph of surface of composite particle, M5-F0.5



Polymerization continues until the emulsifier concentration becomes lower than the CMC. Thus, the oligomeric radicals of initiator seems to capture the well dispersed Fe_3O_4 particles in the polymerization medium, i.e., an aqueous phase, resulting in the new polymer spheres containing Fe_3O_4 particles, i.e., smaller composite particles, as shown in Fig. 8. Figure 10 shows the surface of Ps particles covered with smaller composite particles. It was empirically determined that the weight ratio of Ps/Fe_3O_4 particles must be about 1/0.5 and Ps/monomer, 1/5 ~ 10 in order to obtain a uniform coating state on the whole surface of Ps.

Conclusion

Polystyrene-Fe_3O_4 composite microspheres of core-shell type were obtained by applying seeded polymerization in the presence of seed particles and modified Fe_3O_4 particles. The present heterogeneous polymerization provides the possibilities of synthesizing monodispersed composite microsphere in a variety of combination.

Acknowledgment The authors are grateful to Toda industrial Co., Ltd. for valuable discussions.

References

1. Caris CHM, Kuijpers RPM, van Herk AM, German AL (1990) Makromol Chem Macromol Symp 35/36:535
2. Nishizawa TM, Senna M, Kuno H (1983) J Material Sci 181:346
3. Alonso M, Satoh M, Miyanami K (1989) Powder Technology 59:45
4. Kaye BH (1992) Kona 10:65
5. Tokuoka K, Senna M, Kuno H (1986) J Material Sci 21:493
6. Tanaka M, Hayashi K (1990) J Material Sci 25:987
7. Rios L, Hidalgo M, Cavaille JY, Guillot J, Guyot A, Pichot C (1991) Colloid Polymer Sci 269:812
8. Okubo M, Ikawasaki Y, Yamamoto Y (1991) Colloid Polym Sci 269:217
9. Sang Z, Poehlein GW (1989) J Colloid Sci 128:501
10. Marciniec B, Krysztafkiewicz A, Domka L (1983) Colloid Polym Sci 261:306
11. Imae T, Muto K, Ikeda S (1991) Colloid Polym Sci 269:43
12. Kar P Lok, Christopher K Ober (1985) Can J Chem 63:209
13. Meguro K, Esumi K (1991) Shikizai 64:378
14. Arshady. R (1992) Colloid Polym Sci 270:717
15. Christopher K, Ober, Kar P Lok (1987) Macromolecules 20:268
16. Do Ik L (1990) Makrormol Chem Macromol Symp 33:117
17. Eliseeva VI, Ivanchev SS, Kuchanov SI, Levedev AV (1981) Emulsion polymerization and its applications in industry, Consultants Bureau • New York and London
18. Robb JD (1969) J Polym Sci partA-1 7:417
19. Smith WV, Ewart RH (1984) J Chem Phys 16:592