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Preparation of submicron magnetic latex by miniemulsion polymerization

Yoshitaka Ayusawa, Mayuko Takasu, Toshifumi Shiroya*,
Munehiro Sakamoto* and Haruma Kawaguchi**

Graduate school of Science & Technology, Keio University
Fax: 81-45-566-1563, e-mail: haruma@applc.keio.ac.jp
*Yokohama Research Center, Mitsubishi Chem. Co.

Stable, monodisperse, submicron-sized, magnetite/polymer composite particles with high magnetization were obtained by miniemulsion polymerization using a commercialized magnetic fluid. Magnetite charged into polymerization system was efficiently encapsulated in the particles up to 32%. Simultaneous use of water-soluble and oil-soluble initiators gave the best results in terms of polymerization rate and efficiency of magnetite encapsulation.

Key words: magnetic particle, composite particle. miniemulsion polymerization, encapsulation, nanosphere

1. INTRODUCTION

Magnetite-containing, monodisperse polymer particles have attracted much attention because of their applicability to huge uses such as opto-electrical, rheological, and medical uses. Most of commercialized magnetic particles are of micron-meter order in size [1]. Some trials to obtain smaller magnetic particles have been done eagerly because such particles do not settle down spontaneously, and are expected to find more applications. Miniemulsion polymerization is a useful method to prepare sub-micron composite particles in which hydrophobic materials are encapsulated due to its unique mechanism (Fig. 1). Magnetite nanoparticles are supposed to be encapsulated in a particle if the surface of magnetite nanoparticles is sufficiently hydrophobized.

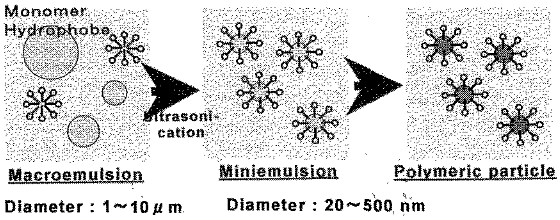


Fig. 1 Process of miniemulsion polymerization in which each monomer miniemulsion droplet is converted to polymer particle

Ramirez and Landfester tried to create composite particles of deca-nanometers containing by more than 15 wt% magnetite by miniemulsion polymerization [2]. But they did not succeed in getting composite particles that satisfy their criteria and adopted a modified miniemulsion polymerization. In their modified miniemulsion polymerization, monomer miniemulsion and magnetite miniemulsion were prepared separately, then mixed, and co-sonicated to obtain stable composite miniemulsion. Finally they could prepare several deca-nanometer-sized particles containing even more than 30wt% magnetite.

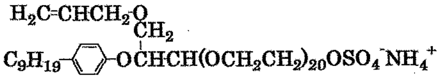
We report here that submicron-sized monodisperse, uniform particles containing more than 30wt% magnetite can be obtained by direct miniemulsion polymerization. This article presents the suitable conditions to prepare such particles and especially argues the role of initiators having different hydrophobicity.

2. EXPERIMENTAL

Materials

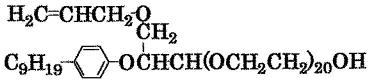
Styrene and glycidyl methacrylate were purchased from Wako Chemicals Co. and purified by distillation at 46 ℃ /21.5mmHg, and 33 ℃ /2mmHg, respectively. Four kinds of initiators, potassium peroxosulfate (KPS), ammonium peroxosulfate (APS), 2,2'-azo(bis-iso-butyronitrile) (AIBN) and benzoyl peroxide (BPO) were also purchased from Wako Chemicals Co. Only KPS was recrystallized from water at 40℃ and the others were used without further purification. Sodium dodecylbenzenesulfonate (DBS, Tokyo Kasei Industry Co.) and two kinds of reactive surfactants, SE-20N and NE-20 (Asahi Denka Chemicals Co., shown below) were used as received.

SE-20N



$$C_9H_{19}-C_6H_4-OCH(CH_2OCH_2CH{=}CH_2)CH(OCH_2CH_2)_{20}OSO_4^-NH_4^+$$

NE-20



$$C_9H_{19}-C_6H_4-OCH(CH_2OCH_2CH{=}CH_2)CH(OCH_2CH_2)_{20}OH$$

Hydrophobes, hexane (HX, Tokyokasei Industry Co.), dodecane (DD, Tokyo Kasei Industry Co.) and hexadecane (HD, Junsei Chemicals Co.) were used without further purification.

Following hydrophobic magnetic fluids were used as received. Both contain magnetite fine particles of about 10 nm diameter.

HC-50 (Taiho Industry Co.) magnetite content: 50wt%, medium: kerosene

HX-20 (Sigma High Chemicals Co.) magnetite content: 20wt%, medium: hexane

An ammonia solution (28-30wt%, extra pure) (Junsei Chemicals Co.) was used without further purification. Doubly distilled water was used in whole aqueous systems.

Miniemulsification

Monomer including magnetite and hydrophobe was added to an aqueous solution of surfactant in a beaker. The tip of an ultrasonicator VP-30S (Titec Co.) was put into the mixture and ultrasonication was performed for different periods of time (3min – 15min) at the maximum power (300W) of the instrument. The extent of miniemulsification was assessed by measuring the surface tension, which is low when miniemulsification is insufficient and increases with the period of ultrasonication time which increases the total surface area of droplets in miniemulsion.

Miniemulsion polymerization

The miniemulsion prepared in the manner mentioned-above was poured into a round bottom flask, equipped with a stirrer, a condenser, a nitrogen inlet and a thermometer. After purging air with nitrogen in the flask, an initiator solution was added into the miniemulsion with a syringe. The polymerization thus started was continued for 24 hr at 60 or 70℃. The resulting composite particles separated from the aqueous medium with the aid of a magnet or, if the magnetic force was insufficient for the separation, with the aid of gravimetric force using a centrifugal separator. The serum was decanted and the particles were re-dispersed. This purification process was repeated for three times.

Characterization of latex

The hydrodynamic sizes of monomer droplets and polymer particles were measured by dynamic light scattering using a LPA3000/3100 (Otsuka Electron Co.). Percent of conversion was measured as a function of polymerization time by gravimetric method. Transmission and scanning electron micrographs were obtained using a HU-12 and S-4700 electron microscopes, respectively, to determine the size and observe the shape of solid particles. The distribution of magnetite in a composite particle was observed on a electron micrograph of ultra-thin section of the composite particle. The content of magnetite in composite particles was determined by thermo-gravimetry.

3. RESULTS AND DISCUSSION

Miniemulsification

MIniemulsification was carried out using a VP-30S ultrasonicator under various conditions in terms of the kind and amount of hydrophobe, the power and period of sonication time, etc. to find the best condition to obtain stable miniemulsions. Measuring the size of monomer droplets in miniemulsion is generally difficult but, in the miniemulsion system prepared by using SE-20N, the size could be measured by dynamic light scattering (DLS). The DLS data showed us that the size of hexadecane (HD, hydrophobe)-containing styrene (St) monomer droplets (hydrophobe/monomer = 10^{-2} – 10^{-1} (molar basis)) prepared by ultrasonication for 8 min increased gradually but the change was less than 20 % without any phase separation even after 30 days incubation at room temperature. As to the period of ultrasonication time, 8 min was appropriate because too short ultrasonication leaves excess of surfactant as micelles and too long ultrasonication causes segregation of monomer phase. So the ultrasonication using an ultrasonicator VP-30S with full power scale for 8 min was employed for the preparation of miniemulsion hereafter.

Miniemulsion polymerization without magnetite

To confirm that polymerization takes place in each monomer droplet to convert it to an individual polymer particle in our polymerization apparatus, the sizes of monomer droplets before polymerization and polymer particles after polymerization were measured in several systems. The sizes were almost unchanged or rather slightly increased during polymerization in the systems composed of St/SE-20N/hexadecane (HD)/water/KPS = 3.0g/0.03g/(0.12 – 0.96)ml/18ml/0.05g. For example, in the system containing 0.12ml HD, the diameters of droplets and particles were 157.9 and 165.6, respectively, and, in the system containing 0.96ml HD, the diameters of droplets and particles were 192.0 and 204.5, respectively. These indicate that the number of particles may decrease by 10% or so through the polymerization although the results may change if the miniemulsion contains magnetite.

Dodecane (DD) exhibited a similar effect with HD as a hydrophobe. For example, both miniemulsions possessed high surface tension, indicating that the surfactant was used up to cover the huge surface area of a large amount of small droplets. But a little difference was observed when miniemulsion polymerization was carried out using small amounts of DD and HD. The size of polymer particles became smaller than that of monomer droplets if the amount of DD was small. This was not the case in HD system as mentioned above. The result implied that DD has lower ability as hydrophobe than HD and allows the monomer molecules to escape from the droplets to aqueous phase and form new particles. Therefore, HD was favorably used for the miniemulsion polymerization hereafter.

Effect of magnetic fluids employed for miniemulsion polymerization

Two kinds of magnetic fluids were employed for the preparation of magnetic latex by miniemulsion polymerization. Both magnetic fluids were organic solvent systems where magnetite was stabilized with some surfactants having low hydrophile/lypophile balance although the true character of surfactants was obscure. One magnetic fluid (HC-20) contained 20wt% magnetite in hexane and the other (HX-50) 50wt% in kerosene. Miniemulsion polymerizations using two magnetic fluids gave different results. The inclusion of HX-50 magnetite in the particle proceeded more efficiently than that of HC-20. The latter system resulted in the formation of magnetic latexes with broad size distribution as well as an appreciable amount of aggregates. Kerosene has a much higher boiling temperature (b.p. 150-250℃), higher viscosity, and lower solubility in water than hexane (b.p. 68℃). These characteristics suggested that HX-50 is a better hydrophobe than HC-20, or unknown ingredients in both magnetic fluids may contribute to the difference.

Even HX-50 however did not give sufficient results to prepare a magnetic latex and formed some aggregates. Therefore, kerosene is not the best hydrophobe but is better to be replaced with some other. Hexadecane was selected as the better hydrophobe. In this polymerization system, about 60% of kerosene in HX-50 was evaporated and the concentrated magnetic fluid was mixed with monomer and a certain amount of hexadecane, followed by miniemulsification. Polymerization proceeded smoothly with the recipe shown in Table Ⅰ.

Table Ⅰ. Typical recipe for composite particle formation by miniemulsion polymerization.

St	HC(conc)	DBS	HD	water	APS
3	1.3	0.06	0.23	15	0.05 (g)

polymerization temperature: 60°C
HC(conc): concentrated HC-50

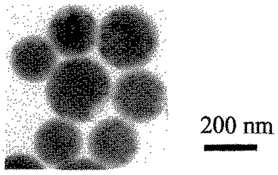


Fig. 2 Magnetic particles obtained with the recipe shown in Table Ⅰ.

The conversion was over 90% and the number average diameter of the particles was 276nm. The TEM view of the particles are shown in in Fig. 2. A number of fine magnetite nanoparticles are observed in the polymer particles.

Effect of initiator

It has been reported that the kind of initiators does not significantly affect the kinetics of miniemuslsion polymerization and the resulting latex. In the preparation of magnetic latex by miniemulsion polymerization, the effect of initiators was studied by using AIBN and APS. Experimental results indicated that magnetite inclusion efficiency was better in APS system than in AIBN system, but the attainable conversion was higher in AIBN system than in APS system, as shown in Fig. 3.

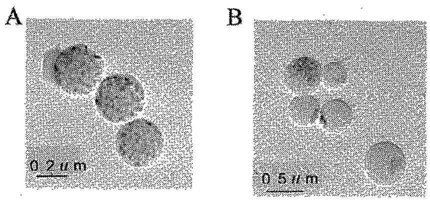


Fig. 3 Magnetic particles obtained by using different Inititors, A: ammonium persulfate, B: azobisisbutironitrle.

In AIBN system, radicals were formed in each droplet and polymerization seemed to proceed rather preferentially inside first and then extend to outside. This resulted in the high polymerization rate as well as the segregation of magnetite to the outside of particle. Moreover chain transfer reaction to monomer followed by escape of radicals to aqueous phase takes place and might cause broadening of size distribution of particles. On the contrary, polymerization in APS system takes place preferentially in the outer layer of droplets because of the hydrophilic nature of initiator radicals. In such a case, radicals are supposed to have less chance to diffuse into the inside of droplets. Therefore, conversion leveled off at a relatively low percent of conversion and magnetite was sent to the inside of droplets. During the slow polymerization, polymerizing particles might scavenge unpolymerized monomer droplets to decrease the number of final particles. To overcome the disadvantage of AIBN system, that is, ill morphology, and the disadvantage of APS system, that is, low percent of conversion, a mixed initiator system was employed. When the polymerization was carried out by using AIBN in the monomer phase and APS in the aqueous phase, the percent of conversion increased smoothly during polymerization reaction and, as shown in Fig. 4, the morphology of particles was improved.

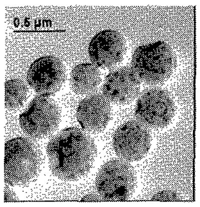


Fig. 4 Magnetic particles obtained by using mixed Initiators.

An ultra-thin section of a composite particle is observed by TEM and the view is shown in Fig. 5. It revealed that the particle contained a large amount of magnetite nanospheres but the location of magnetite in the particle seems to be different from that in Fig. 4. The difference is supposed to result from the diffusion of magnetite in the particle during thin-section sample preparation.

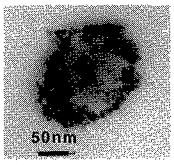
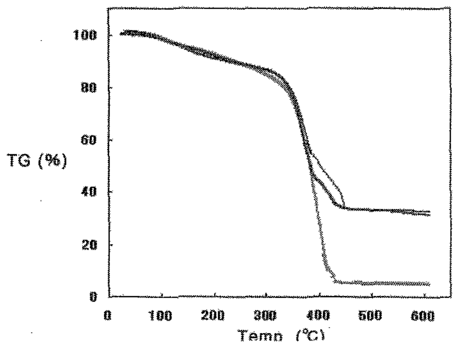


Fig. 5 Ultra-thin section of a magnetite/polymer composite particle.

Separation of magnetic latex particles from the medium by a magnet

The content of magnetite in the particles was measured by thermogravimetry (TG) and the results are shown in Fig. 6, which indicates that all of the particle-composing polymeric and organic materials were decomposed during heating to 350℃. The particles with lowest magnetite content (the lowest curve in Fig. 6) were those prepared by using HX-20. The other two in Fig 6 are the particles obtained by using HC-50 and the contents coincided with the expected values.

Magnetic latex was put into a cell contacting with a magnet and the rate of separation of magnetic particles from the medium was measured from the absorbance change of the sample as a function of time. The results for three kinds of latexes are shown in Fig. 7. It indicated that the particles of larger size and of higher magnetite content are quicker in response to the magnetic force.



Fg. 6 Thermogravimetric curves of magnetic particles.

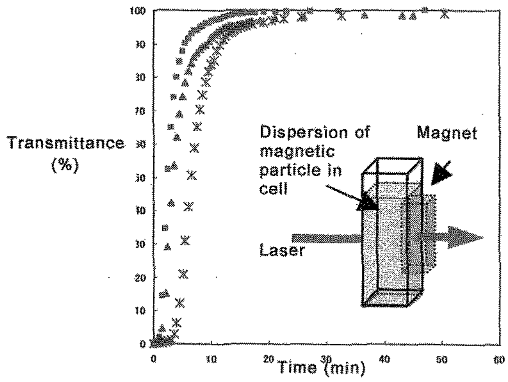


Fig. 7 Recovery of three kinds of magnetic particles with a magnet.

	Diameter (nm)	**Magnetite content (%)**
■	438	18
▲	256	30
*	225	19

Surface modification and protein adsorption

Because it is well-known that the particles whose surfaces were covered with poly(glycidyl methacrylate) (poly-GMA) is less susceptible to protein adsorption [3], the magnetic latex particles were employed for seeded polymerization of GMA. The adsorption of human gamma globulin onto modified particles as well as some other particles was determined. The most hydrophobic particle, polystyrene particle, adsorbed a largest amount of globulin. Poly-GMA-masked magnetic particles adsorbed the least amount of globulin among the particles examined. There are two reasons for this. One reason is the bio-inert nature of poly-GMA and the other is the negative charge of particles. The latter causes electrorepulsive force between the particle and globulin molecule to suppresses the adsorption under the condition for adsorption experiment (pH 7.3).

4. CONCLUSIONS

Stable, monodisperse, submicron-sized magnetite/polymer composite particles were successfully prepared by miniemulsion polymerization using a commercially available magnetic fluid. Almost all the charged magnetite was encapsulated and the maximum content of magnetite in the particles was over 30wt%. Initiator played a crucial role in controlling the distribution of magnetite in the particles. The submincron-sized particles containing 30% magnetite were smoothly collected from the dispersion with a magnet.

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