

# Preparation of Magnetic Latex Particles by Emulsion Polymerization of Styrene in the Presence of a Ferrofluid

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## SYNOPSIS

Magnetic latex particles were prepared by the emulsion polymerization of styrene at 70°C in the presence of a commercial ferrofluid containing surfactant-stabilized magnetite particles in the aqueous phase or its modification by ultrafiltration, using potassium persulfate as an initiator. The effects of diversified variables such as the amounts of initiator, monomer, and additive (calcium chloride and fluorescent dyes) on the polymerization reaction and particle characteristics were investigated. The general polymerization features were analogous to those of ordinary emulsion polymerizations. Transmission electron microscopy revealed that when the commercial ferrofluid was used the magnetite particles localized in the latex particles and the magnetite content varied from particle to particle and that when the ferrofluid was used after ultrafiltration the magnetite particles were dispersed well in the latex particles. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

A variety of cell-separation methods have been used to isolate specific cells from mixed-cell populations. Conventional procedures are based on physical properties of cells such as size, surface charge, density, and adhesiveness. However, these do not necessarily meet the requirements of cell biologists because of their complex and time-consuming procedures and insufficient specificity. Furthermore, they present difficulties in their application to large-scale cell preparation.

Recent developments in monoclonal antibody techniques have made it possible to separate cells based on the differences of specific cell-surface antigens. Flow cytometry and panning techniques are representatives. However, these are still not satisfactory to thoroughly alleviate the above problems.

Since magnetic polymeric microspheres can be easily collected with application of a magnetic field, coupling of appropriate ligands to such microspheres

provides an effective tool to achieve rapid, simple, and specific cell separation even in large-scale preparation.<sup>1</sup> Accordingly, such immunomagnetic particles have also been applied to cell labeling, radio immunoassay, enzyme immunoassay, affinity chromatography, phagocytosis, site-specific chemotherapy, and so forth.<sup>1</sup>

Coating or encapsulation of magnetic particles with preformed polymers is the oldest and simplest method to prepare magnetic microspheres. Various types of magnetic microspheres based on natural polymers,<sup>2</sup> synthetic polymers,<sup>3</sup> and composites thereof<sup>4</sup> have been prepared by this method. Another method is vinyl polymerization initiated either chemically<sup>5</sup> or by  $\gamma$ -ray irradiation<sup>6</sup> in the presence of magnetizable particles. Other methods include combinations of two of these methods<sup>7</sup> and polymerization of glutaraldehyde in the presence of a ferrofluid.<sup>8</sup> The particles obtained are, however, not ideally suitable for immunological and medical research, because of the inherent inhomogeneity in particle size and content of magnetic particles as well as distortion of the particles. Obviously, these do not permit uniform behavior of the particles in a solution and a magnetic field.

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Incorporation of magnetic particles into microspheres at the time of emulsion polymerization should be more suitable in this respect. Solc<sup>9a</sup> prepared magnetic latex particles by emulsion polymerization of hydrophobic monomers in the presence of a freshly prepared Fe<sub>3</sub>O<sub>4</sub> ferrofluid. At about the same time, Ugelstad et al.<sup>10,11</sup> developed a novel method to prepare magnetic microspheres based on their own methods of "activated" swelling, namely, the two-step swelling method,<sup>12-16</sup> and applied the magnetic microspheres to immunological and medical research as well.<sup>1c,1f-i</sup>

The Ugelstad method for the preparation of magnetic polymeric microspheres has now been well established and commercial products are available.<sup>17</sup> However, no detailed studies have so far been reported concerning the preparation of magnetic microspheres by the emulsion polymerization in the presence of a ferrofluid.<sup>9</sup>

In some of these studies,<sup>6a,8a</sup> magnetic microspheres were also tagged with a fluorescent dye by the FITC method. In general, when incorporated into microspheres, a fluorescent dye functions as a visual marker of the particles under a fluorescence microscope, and, hence, their medical and immunological applications can be widely expanded.

We have independently been investigating the preparation of fluorescent and/or magnetic latex particles, intending to use them in immunological studies<sup>18-24</sup> such as phagocytosis and cell sorting as well as in the magnetic targeting therapy of cancer. In a previous paper,<sup>24</sup> we briefly reported on the preparation of magnetic polymeric latex particles by the emulsion polymerization of vinyl monomers such as styrene (St) and methyl methacrylate in the presence of a ferrofluid and, in some cases, a fluorescent dye and also, in detail, on their characterization by thermal analysis. The present paper discusses the preparation of magnetic poly (St) latex particles by the same method in more detail.

## EXPERIMENTAL

### Materials

Styrene was obtained from Wako Pure Chemicals Industries Co. and distilled under reduced pressure shortly before use. Potassium persulfate, reagent grade, was purchased from Koso Chemical Co. and used without further purification. Water was purified by ultrafiltration of ion-exchanged water using a NANO-pure, D2600 (Barnstead, Iowa). Ferricolloid W-35<sup>®</sup> (magnetite content: 35%) was obtained from

Taiho Industries Co., Tokyo, and used as received. Fluorescent dye, *N*-butyl-4-butylamino-1,8-naphthalenedicarboximide (FD-2, Ref. 24), was a gift from Nippon Kayaku Co., Takasaki, Gunma, and used without further purification. Other chemicals were reagent grade and used as received.

### Ultrafiltration of Ferrofluid

The ferrofluid was diluted with pure water 30 times its weight. The diluted ferrofluid, 800 g, was ultrafiltered, using an ultrafiltration apparatus, UF-Labo, Tosoh, Tokyo, and a Tosoh membrane, UF-1000PS. After 1 h, about one-half of the aqueous phase was filtered off and pure water was added up to the initial level. The same procedure was repeated every 1 h, taking 10 h in all. The final conductivity of the filtrate had decreased to practically level off. The concentration of the ultrafiltered ferrofluid was adjusted to a magnetite content of 35%.

### Polymerization

Emulsion polymerizations were carried out in a manner similar to our previous method.<sup>18</sup> Required amounts of St, ferrofluid, and additives were placed in a 120 mL glass pressure bottle. The total volume of the reaction mixture was adjusted to 60 mL by addition of water. After having been gently bubbled with a fine stream of nitrogen for ca. 5 min, the mixture was stirred for 1 h with constant horizontal and elliptic shaking (8 × 9 cm in axes and 98 rpm) using a Taiyo incubator, Model XY-III. The mixture was then heated to 70°C and the initiator (potassium persulfate) solution was added. Polymerization was allowed to proceed at 70°C for 20 h with shaking. The coagulum was removed by filtration through a filter paper (Toyo Filter Paper No. 2) and dried at 80°C. The latex thus obtained was analyzed as described below.

### Latex Yield

The latex yield was determined by the method described in a previous paper.<sup>24</sup>

### Transmission Electron Microscopy

A drop of a latex diluted with water was mounted on a collodion film and dried at room temperature. TEM observation of the latex particles was then carried out with use of a JEOL transmission electron microscope, Model JEM-100B, at a voltage of 10 kV.

## Particle Diameter

The average diameter of latex particles was obtained by transmission electron microscopy, followed by statistical treatment.

## Magnetite Content

The weight percentage of the residue remaining from a dried latex sample after thermal analysis up to 900°C in nitrogen is given as the magnetite content, assuming that the residue is pure magnetite. The details of the analytical method have been discussed in our previous paper.<sup>24</sup>

## RESULTS

### Emulsion Polymerization

Emulsion polymerizations of St were carried out in the presence of the commercial ferrofluid (Ferri-colloid W-35; Fc), using potassium persulfate (KPS) as an initiator and without any added surfactants but those contained in Fc.

According to the manufacturer, Fc is a colloid of magnetite particles in the aqueous phase and is prepared by the method of Shimoiizaka et al.<sup>25</sup> The surface of magnetite particles is coated first with a monolayer of sodium oleate by strong chemisorption and then with a monolayer of sodium dodecylbenzenesulfonate (SDBS) by weak physisorption. The aqueous phase contains a large amount of SDBS as emulsifier to stabilize the second coating layer and glycols such as ethylene glycol and glycerol as antifreezing agents. Therefore, the magnetic particles have sulfonate groups on their surface, which allows the particles to remain in the colloidal state in the aqueous phase.

### Effect of the Weight Ratio of Fc to St ( $x_w$ )

The effect of the weight ratio of Fc to St,  $x_w$ , on the emulsion polymerization reaction has already been reported in our previous paper.<sup>24</sup> The main conclusions were the following: (1) Complete incorporation of magnetite particles into latex particles occurred at an  $x_w$  value below ca. 0.8. (2) At an  $x_w$  value of ca. 0.05, the latex yield was minimum, whereas the coagulum yield was maximum. (3) The particle diameter monotonously decreased with increase in  $x_w$ : 5890 Å at  $x_w = 0$  and only 620 Å at  $x_w = 0.66$ . (4) The magnetite content in the latex particles ( $x_w < \text{ca. } 0.8$ ) was close to that calculated for the ideal

emulsion polymerization<sup>24</sup> and, hence, is primarily determined by  $x_w$ . Thus, in the following, all the polymerization experiments were carried out at an  $x_w$  value of 0.44, unless otherwise stated.

### Effect of the Amount of Initiator

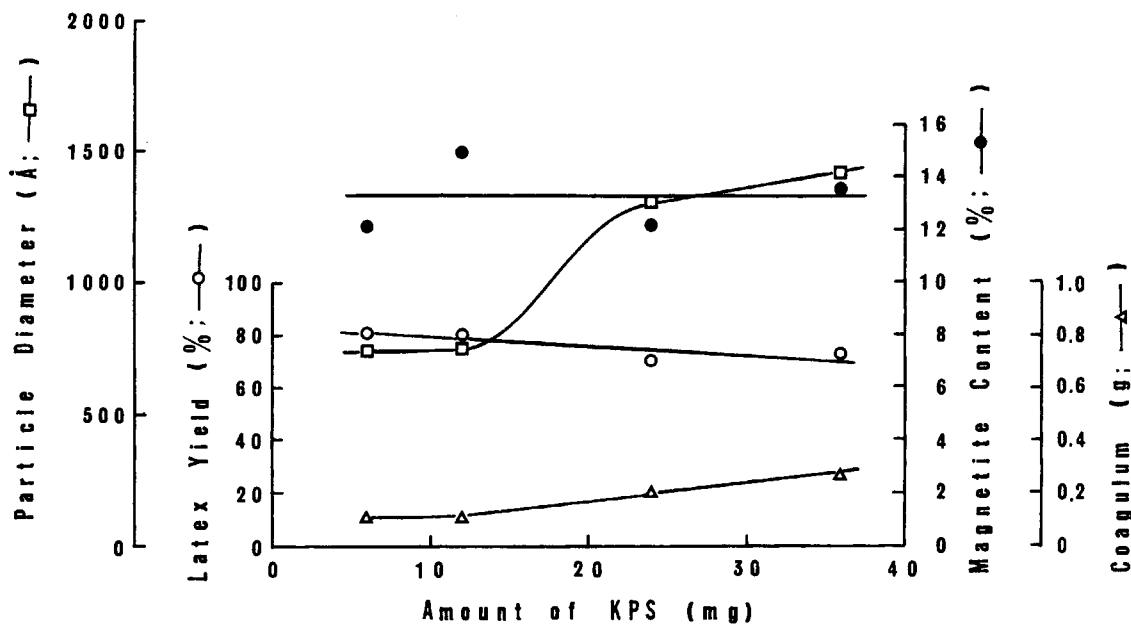
Figure 1 shows the effect of the amount of KPS on the formation of magnetic poly(St) latex particles at an  $x_w$  value of 0.44, a constant amount of calcium chloride being added as an additive. The latex yield gradually decreased with increase in the amount of the initiator, and the decrease is compensated by the gradual increase in the formation of the coagulum. Even in the presence of Fc, the particle diameter increased with increase in the initiator amount as in the cases of ordinary emulsion polymerizations<sup>26</sup> and ordinary soap-free emulsion polymerization.<sup>27-31</sup> The magnetite content was constant over a wide range of the initiator amount.

In Figure 2 are presented the results of the emulsion polymerizations under the conditions similar to those in Figure 1 but in the presence of fluorescent dye FD-2. The general trend in the variation of the latex yield, particle diameter, and magnetite content with increasing amount of KPS was the same as before, in spite of the presence of the dye. It should be noted that the dye was completely incorporated into the polymeric products and that the addition of the dye considerably reduced the formation of the latex particles and the coagulum.

### Effect of the Amount of Monomer

The emulsion polymerization of St with a fixed amount of KPS was carried out, varying the total amount of Fc and St, while keeping their ratio ( $x_w$ ) at a constant value of 0.44. As depicted in Figure 3, increase in the amount of monomer did not greatly change the latex yield, particle diameter, or magnetite content, but appreciably enhanced the formation of the coagulum.

Figure 4 presents the results of emulsion polymerizations of St in which the ratio of St:Fc:KPS was kept constant ( $x_w = 0.44$ ) and the total amount of the three components was increased in the same volume (60 mL) of the reaction mixture. The latex yield and the magnetite content remained practically constant over a fourfold variation of the amount of the monomer, Fc or KPS. Conversely, the particle size and the formation of the coagulum markedly increased with increase in the amounts of the three components, reflecting the combined effects of KPS (Figs. 1 and 2) and the monomer (Fig. 3).

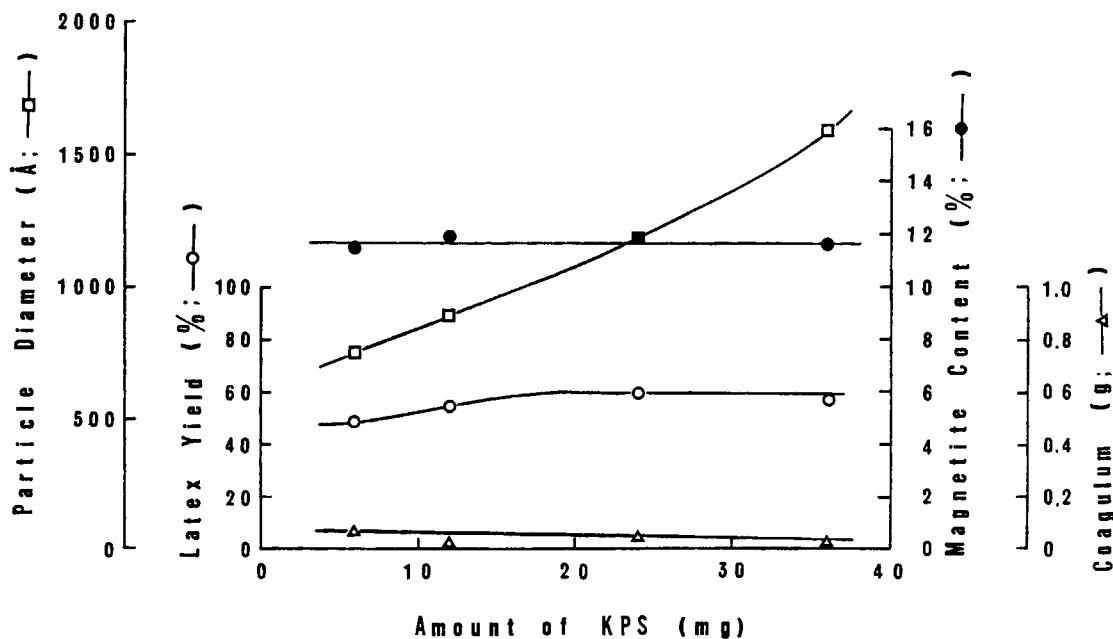


**Figure 1** Effect of the amount of the KPS on the formation of magnetic poly(St) latex particles. Polymerization conditions: St, 6.0 mL; Fc, 2.4 g; calcium chloride, 16 mg; total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.

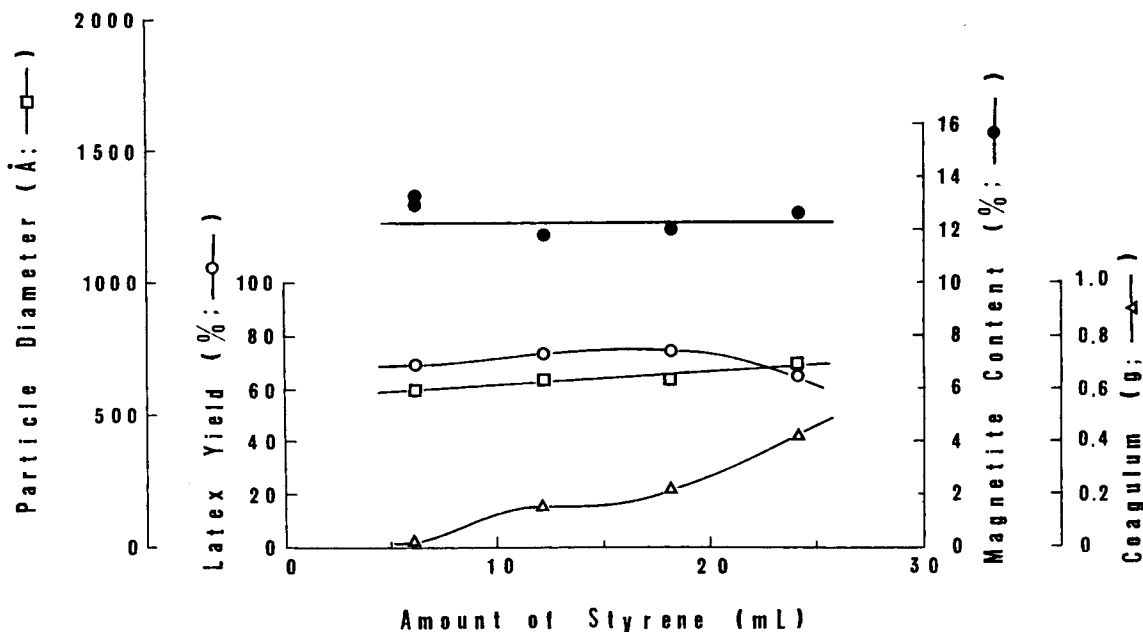
#### Effect of Additives

Calcium chloride was used as an additive for the emulsion polymerizations at  $x_w = 0.44$  with the in-

tention to increase the particle diameter. As shown in Figure 5, the particle diameter and the amount of the coagulum increased markedly, whereas the latex yield decreased dramatically when the amount



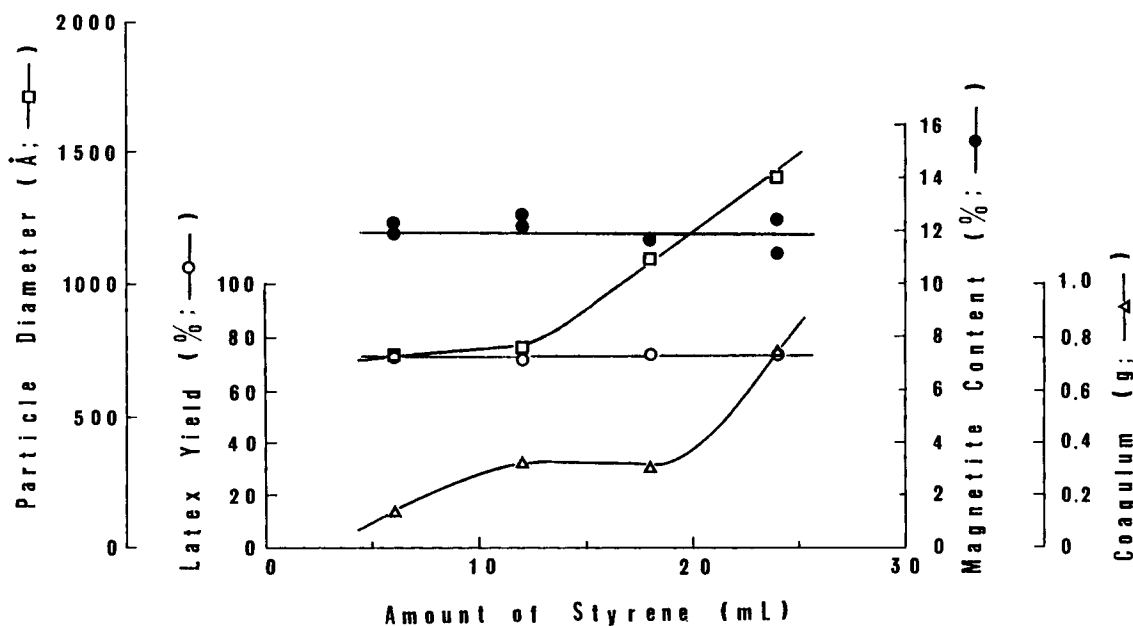
**Figure 2** Effect of the amount of KPS on the formation of magnetic poly(St) latex particles in the presence of fluorescent dye FD-2. Polymerization conditions: St, 6.0 mL; Fc, 2.4 g; calcium chloride, 16 mg; FD-2, 18 mg; total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.



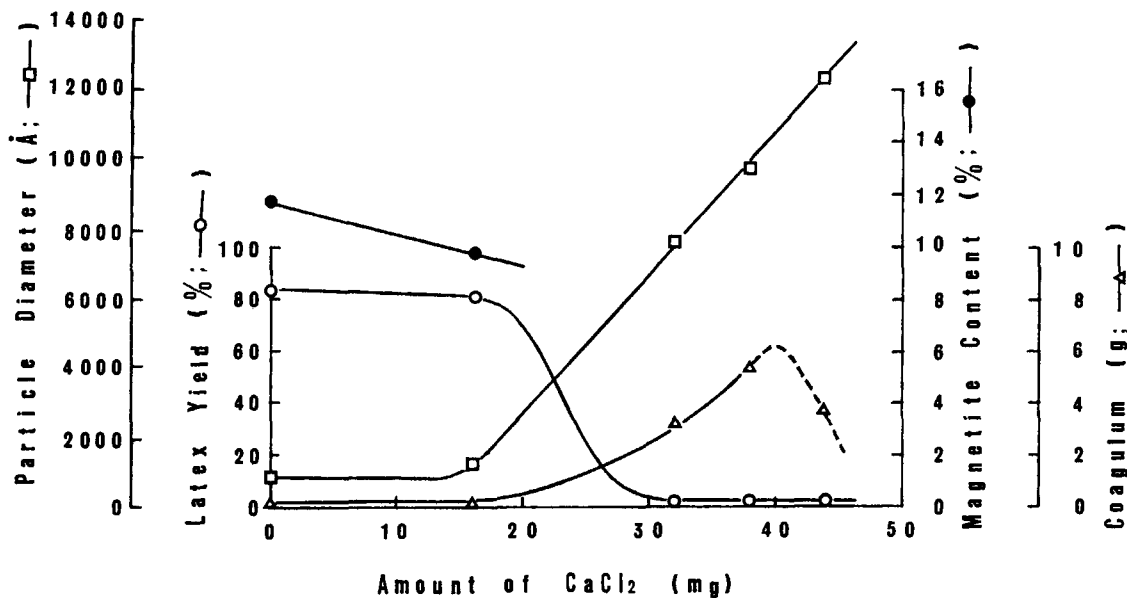
**Figure 3** Effect of the amount of St on the formation of magnetic poly(St) latex particles at a fixed ratio of St to the ferrofluid. Polymerization conditions: weight ratio of Fc to St ( $x_w$ ), 0.44; KPS, 12 mg; total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.

of the salt was increased. These results are analogous to those obtained in ordinary emulsion polymerizations<sup>32</sup> in the presence of a surfactant as well as in the ordinary soap-free emulsion polymerizations.<sup>27-31</sup>

At a very high level of salt, neither the latex nor the coagulum could be formed. Thus, addition of calcium chloride does not promote the formation of large magnetic latex particles in high yield.



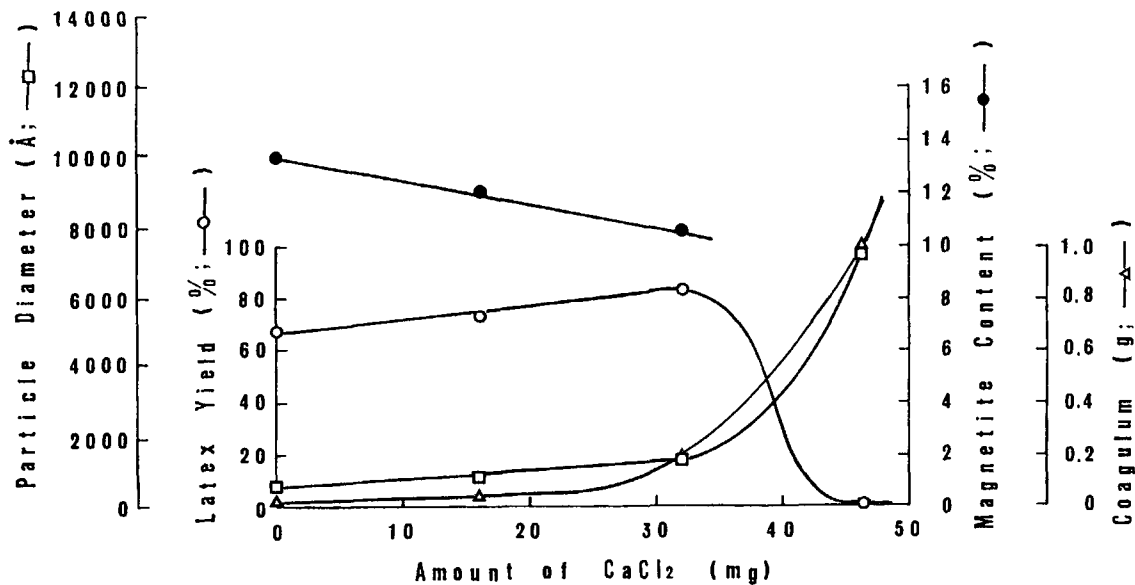
**Figure 4** Effect of the amount of St on the formation of magnetic poly(St) latex particles at a fixed ratio of St to Fc to KPS. Polymerization conditions: ratio of St (mL) to Fc (g) to KPS (mg) = 1:0.4:2, total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.



**Figure 5** Effect of the amount of calcium chloride on the formation of magnetic poly (St) latex particles. Polymerization conditions: St, 6.0 mL; Fc, 2.4 g; KPS; 12 mg, total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.

Figure 6 shows the results of the same polymerization reactions in the presence of fluorescent dye FD-2. The changes in latex yield, particle diameter, and magnetite content with increasing calcium chloride are analogous to those observed in the absence of the dye. Although in the absence of calcium

chloride the addition of the dye reduced the latex yield, the presence of both calcium chloride and the dye appears to make the latex more stable, as judged by the sustained latex yield at higher calcium chloride concentrations, the particle diameter, however, becoming considerably smaller as a whole. In har-



**Figure 6** Effect of the amount of calcium chloride on the formation of magnetic poly (St) latex particles in the presence of fluorescent dye FD-2. Polymerization conditions: St, 6.0 mL; Fc, 2.4 g; KPS, 12 mg; FD-2, 18 mg; total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.

mony with this, the formation of the coagulum was extremely reduced as a whole, although increasing the amount of calcium chloride did enhance the formation of the coagulum (compare Fig. 6 with Fig. 5).

**Effect of Ultrafiltered Ferrofluid**

To completely comprehend the present emulsion polymerization, it is desirable to make the polymerization system simpler. Then, it would be better to remove free surfactants and other additives from Fc than to add something, such as calcium chloride, in the polymerization system. Therefore, we prepared ultrafiltered Fc.

Figure 7 shows that, when the emulsion polymerization was carried out in the presence of fluorescent dye FD-2 using ultrafiltered Fc and large amounts of KPS (compare Fig. 7 with Fig. 2), magnetic latex particles with larger diameters, from 6,150 to 10,970 Å, were obtained, although the latex yields were disappointingly low.

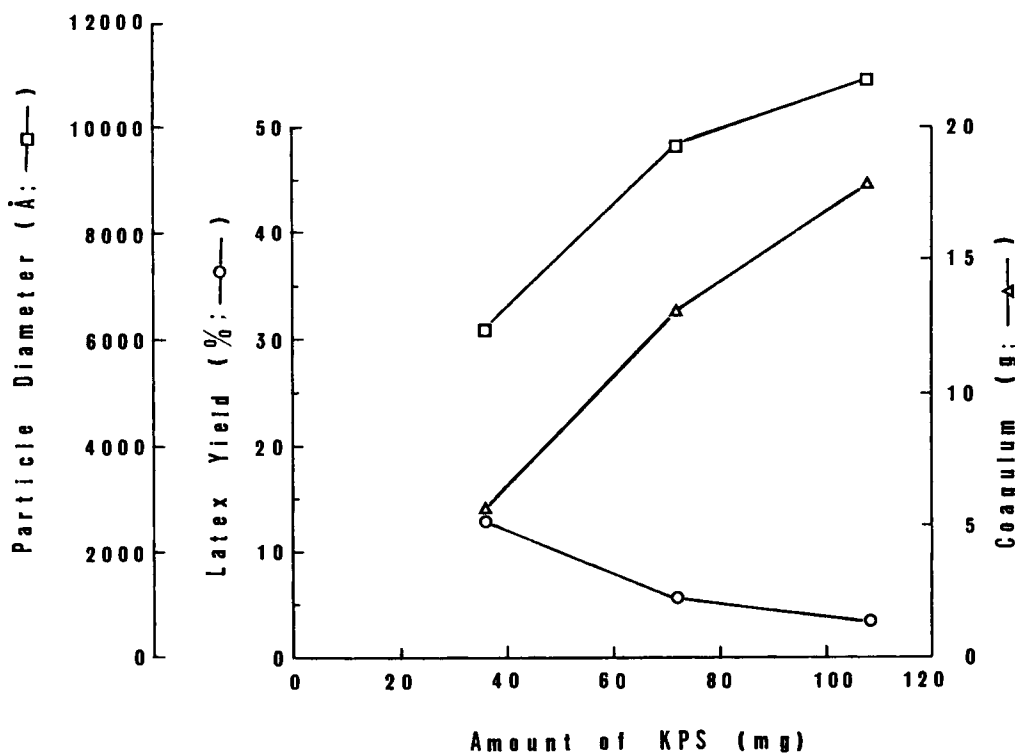
Similarly, as depicted in Figure 8, the use of the ultrafiltered Fc under the conditions similar to those in Figure 4 made it possible to produce latex particles

with an average diameter of up to 8500 Å, but the latex yield was as low as 17%. Most of the remaining monomer was converted into the coagulum. The magnetite contents were 11.9 and 8.4% for the latex particles obtained with the use of 12 and 18 mg of KPS, respectively.

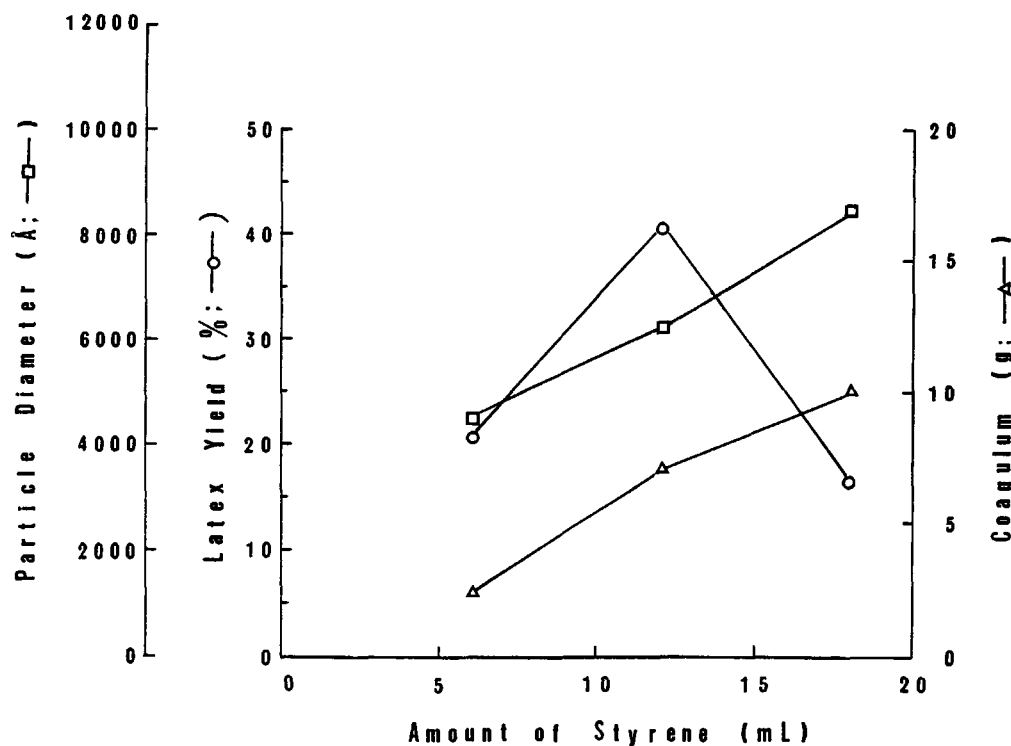
**TEM Characterization of Magnetic Latex Particles**

Figure 9(a) shows the transmission electron microscopy (TEM) photomicrograph of the commercial ferrofluid. Each magnetite particle is approximately 100 Å in diameter. The TEM photomicrograph of the ultrafiltered ferrofluid was almost the same as that of Figure 9(a).

The magnetic fluorescent latex particles looked brown due to the presence of magnetite and the dye. When the same particles were observed through a fluorescence microscope, their strong fluorescence permitted us to easily observe them even when they were incorporated into cells such as macrophages.<sup>21</sup> Figure 9(b) presents the TEM photomicrograph of a representative magnetic poly(St) latex sample prepared in the presence of the commercial ferro-



**Figure 7** Effect of the amount of KPS on the formation of magnetic poly(St) latex particles using the ultrafiltered Fc. Polymerization conditions: St, 18.0 mL; ultrafiltered Fc, 7.2 g; FD-2, 54 mg; total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.



**Figure 8** Effect of the amount of St on the formation of magnetic poly(St) latex particles using the ultrafiltered Fc. Polymerization conditions: ratio of St (mL):ultrafiltered Fc (g): KPS (mg) = 1:0.4:2; total volume, 60 mL; reaction temperature, 70°C; reaction time, 20 h.

fluid. The magnetite particles, which can be recognized as black particles, are well incorporated in the latex particles but are localized near the surface of the particles. Each latex particle contains, more or less, some amount of magnetite particles. The TEM observation of the latices prepared under various conditions revealed that when  $x_w$  was smaller than ca. 0.8 all the magnetite particles were occluded in the latex particles.<sup>24</sup>

Figure 9(c) illustrates the TEM photomicrograph of a magnetic latex sample prepared using the ultrafiltered ferrofluid. Significantly, the magnetite particles are dispersed much better inside the latex particles as compared to those prepared in the presence of the commercial ferrofluid.

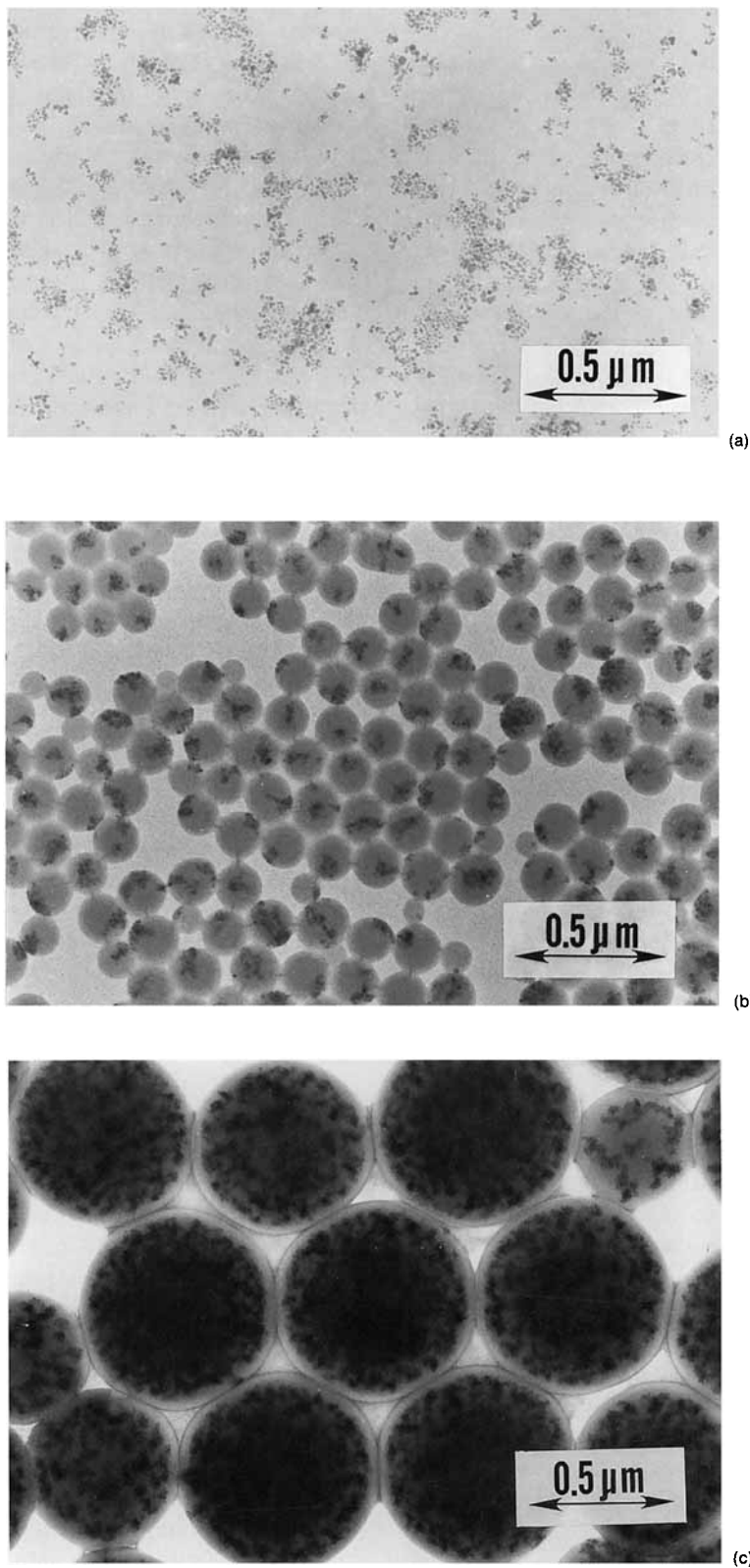
The uniformity of the size of the latex particles prepared in the presence of Fc greatly depended on the reaction conditions and was, in many cases, worse than that in Figure 9(b) and that of the latex particles obtained by ordinary soap-free emulsion polymerization (see below).<sup>27</sup> The coefficient of variation of the particle-size distribution ( $f$  = standard deviation/average particle diameter) was, in general, large when the latex sample was prepared in the presence of a small amount of surfactant,

namely, with use of a small amount of Fc or with use of the ultrafiltered Fc or when the latex sample was prepared at a high ionic strength.

## DISCUSSION

As we have already reported,<sup>24</sup> the magnetite content in the latex particles formed in the present polymerization system using the commercial ferrofluid is primarily determined by the weight ratio of Fc to St ( $x_w$ ) in the feed, and magnetite particles were completely incorporated into the poly(St) microspheres only when  $x_w$  was smaller than ca. 0.8. In agreement with these conclusions, the magnetite content was, in general, independent of the amounts of KPS (Figs. 1 and 2) and the fluorescent dye as well as of the diameter of the particles formed. The decrease of the magnetite content on increasing addition of calcium chloride and the difference between the magnetite contents in Figures 5 and 6 cannot be discussed with certainty, since the magnetite contents at high additive levels could not be determined due to the low latex yields and, in general,





**Figure 9** TEM photomicrographs of (a) Fc, (b) magnetic poly(St) latex particles obtained by the use of Fc ( $f = 14\%$ ), and (c) magnetic poly(St) latex particles prepared by the use of the ultrafiltered Fc ( $f = 20\%$ ).

the experimental values of the magnetite contents fluctuate considerably.

In common with the ordinary emulsion polymerization of St with use of KPS,<sup>32</sup> the magnetic latex particles prepared in the presence of Fc have anionic charges on their surface by adsorption of the anionic surfactants and also as initiator fragments at the polymer terminals. Thus, the increase of the particle diameter with increase in the amount of KPS (Figs. 1 and 2) and calcium chloride (Figs. 5 and 6) can be attributed to the increase of the ionic strength of the system.<sup>28,31</sup> The larger increase of the particle diameter with the latter salt is due to the fact that the calcium ion is more strongly adsorbed onto the Stern's electric double layer near the particle surface to effectively reduce the surface charge density and, hence, the growing particles readily coagulate to larger particles. The particle diameter also slightly increased with increase in the amount of the monomer (Figs. 3 and 4), presumably due to the increased opportunity of coagulation of the growing latex particles.

The latex yield was abruptly reduced on increasing the amounts of added calcium chloride (Figs. 5 and 6) and, with use of the ultrafiltered Fc, even of KPS and the monomer (Figs. 7 and 8). Increasing the amount of monomer facilitated the formation of coagulum (Figs. 3, 4, and 8). In general, the yields of the latex and the coagulum are in a complementary relation to each other (Figs. 1, 2, 5, 6, and 7; see also Fig. 1 in Ref. 24), reflecting the stability of the latex under the given polymerization conditions. The decrease of both the latex and the coagulum yield at high calcium chloride concentration (Fig. 5) is ascribed to the destruction of the emulsion by the salts.<sup>29</sup>

Fluorescent dye FD-2, which is soluble in the monomer but insoluble in water and, hence, was completely incorporated into the latex particles, did not do any serious harm to the emulsion polymerization, except that, in the absence of calcium chloride, the dye appreciably decreased the latex yield (compare Fig. 6 with Fig. 5). In the presence of both calcium chloride and the dye, the latex yield gradually increased until destruction of the latex began (Fig. 6). On the other hand, the dye definitely decreased the yield of the coagulum (compare Figs. 2 and 6 with Figs. 1 and 5, respectively). The particle diameter was not influenced greatly (compare Fig. 1 with Fig. 2) or considerably reduced (compare Fig. 5 with Fig. 6) by the addition of the dye. Thus, the dye is considered to behave somewhat like a surfactant and to stabilize the emulsion when combined with calcium chloride.

Other fluorescent dyes such as 3-(2'-benzimidazolyl)-7-diethylaminocoumarin (FD-1, Ref. 24) and Fluorol Red BK® (BASF) could also be incorporated into latex particles. Introduction of a fluorescent function to latex particles had previously been carried out by covalent bonding of a fluorescent dye or its derivative, e.g., by the FITC method.<sup>6a,8a,33</sup> Then, it is obvious that our method is much simpler.

In the present polymerization system using the commercial ferrofluid, it is very difficult to obtain large latex particles with a high magnetite content in high yield,<sup>24</sup> and, besides, in the same latex sample, the magnetite content greatly varies from particle to particle [Fig. 9(b)]. The former and probably the latter also are considered to be due primarily to the surfactants in the aqueous phase of the ferrofluid. In fact, removal of the surfactants and other components in the aqueous phase of the commercial ferrofluid by ultrafiltration effected the increase of the particle diameter up to ca. 11,000 Å (Figs. 7 and 8), which is large enough for biological and medical studies such as DNA<sup>11,34</sup> and cell separations, and better dispersion of the magnetite particles in the latex particles (Fig. 9c). Unfortunately, however, the latex yield was very low when a large amount of KPS or monomer was used (Figs. 7 and 8).

In their preparation of magnetic microspheres by their novel method, Ugelstad et al.<sup>10</sup> formed iron oxides *in situ* in the presence of porous monodisperse microspheres. The magnetizable particles formed were fine and existed homogeneously throughout the particles.<sup>1h,11</sup> Thus, from the viewpoint of various applications of magnetic microspheres, their method may be superior to the present method for the reasons mentioned in the Introduction.

However, the present method using either the commercial or the ultrafiltered ferrofluid and a fluorescent dye<sup>35</sup> at the time of emulsion polymerization is experimentally much simpler as compared with the methods of Rembaum<sup>6a,8a</sup> and Ugelstad,<sup>10</sup> namely, fluorescent dye and magnetite particles can be incorporated into the latex particles in one pot without elaborated procedures. It still remains a problem, however, that the latex yield is low (Figs. 7 and 8) and the particle-size distribution is relatively wide [Figs. 9(b) and (c)].

The mechanism of the present emulsion polymerization in the presence of Fc or an ultrafiltered Fc is far more complex than that of an ordinary emulsion polymerization, because of the additional presence of surfactant-coated magnetite particles and other additives in Fc. Thus, we discuss here only the effect of the weight ratio of Fc to St,  $x_w$ , on the emulsion polymerization of St, which we have al-

ready reported in a previous paper.<sup>24</sup> The results were briefly reviewed at the beginning of the Results section.

As shown in Figure 1 of our previous paper,<sup>24</sup> when a small amount of Fc ( $x_w = 0.055$ ) was added, the latex yield was remarkably low, although high at  $x_w = 0$ . Then, it gradually increased on further addition of Fc. Thus, in the presence of a small amount of Fc, the emulsion would be unstable due to the low concentration of surfactants, and, hence, a large amount of a magnetic coagulum is concurrently formed. The gradual increase in the yield of magnetic latex particles with increase in  $x_w$  could be attributed to the stabilization of the latex by the increasing amount of the surfactants introduced on addition of Fc. This is supported by the decrease<sup>24,32</sup> in the particle diameter and the amount of coagulum with increase in  $x_w$ . Here, it should be noted that, considering the features of Fc described earlier, its addition in the polymerization mixture is not only to increase the amount of magnetite particles but also to increase the amount of the surfactants.

Since the polymerization at  $x_w = 0$  is the so-called soap-free emulsion polymerization, the polymerization mechanism at  $x_w = 0$  should no doubt be different from that for the polymerization in the presence of Fc. In fact, at  $x_w = 0$ , the latex yield was high, and yet the particle diameter was relatively large with a small  $f$  value of 4.8%. This constitutes a big difference from the above-mentioned results at  $x_w > 0$ , where the particle diameter and the  $f$  value monotonously decreased from 4910 Å and 43% at  $x_w = 0.055$  to 620 Å and 1.6% at  $x_w = 0.66$ . The polymerization in this case can be understood according to, for example, the mechanism of Goodall et al.<sup>36</sup> Thus, it is not reasonable to discuss the emulsion polymerization at  $x_w = 0$  in the same way as that at  $x_w > 0$ . In this way, the appearance of the maximum of the coagulum yield and the minimum of the latex yield at low  $x_w$  values<sup>24</sup> can be consistently explained.

As mentioned above, the general features of the present emulsion polymerization are analogous to those of an ordinary emulsion polymerization using a surfactant.<sup>26,32</sup> This is considered to reflect the fact that the magnetite particles of Fc are coated by surfactants and therefore do not affect the polymerization reaction to a significant extent. At present, we are trying to work out the detailed polymerization mechanism and hope to discuss it in a future paper.

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