

Preparation and Characterization by Thermal Analysis of Magnetic Latex Particles

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SYNOPSIS

Emulsion polymerization of styrene and methyl methacrylate in the presence of a ferrofluid was briefly studied. Thermal properties of the resulted latex particles were investigated by TG-DTA analysis. Determination of the residue weight after the thermal analysis that indicated complete decomposition of the organic components was found to be a facile and practical method to determine the magnetite content in the latex particles. The method was applied to magnetic polystyrene latex particles prepared in the presence of various amounts of the ferrofluid. Analysis of the results suggested that the magnetite content in the latex particles is primarily determined by the weight ratio of the ferrofluid to monomer.

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INTRODUCTION

Magnetic polymeric microspheres with functional groups such as hydroxyl and carboxyl groups as well as unfunctionalized ones have been attracting much attention for their potential as tools in immunological and medical research as well as in therapy. They have been applied to the studies of cell labeling, cell separation, phagocytosis, site-specific chemotherapy, radio immunoassay, enzyme immunoassay, affinity chromatography, and so forth.¹ We have also been investigating the synthesis of fluorescent and/or magnetic latex particles, intending to use them in similar studies.²⁻⁶ Recently, preparation of polymeric films containing magnetic particles has been published.^{7,8} A variety of applications may also be envisioned for them.

In these studies, the content of magnetic particles in a magnetic polymeric material is one of the fundamentally important quantities to be measured. Although many papers record the magnetite content in magnetic microspheres, no detailed analytical

method has been described. In addition, preparation of magnetic latex particles by emulsion polymerization in the presence of a ferrofluid has not been investigated in any detail.^{9,10}

Thus, in the present study, emulsion polymerization of styrene and other monomers in the presence of a ferrofluid¹¹ was briefly studied to obtain magnetic latex particles of different types. In some cases, a fluorescent dye, which under suitable conditions should serve as a visual marker through a fluorescence microscope, was also incorporated into the particles.¹² Then, the thermal behaviors of dried latex particles were studied by means of thermogravimetry-differential thermal analysis (TG-DTA), which turned out to be a practical method to determine the average magnetite content in the magnetic polymeric latex particles. A similar method appears to have been applied to poly(methyl methacrylate)-encapsulated inorganic powders, but no methodology has been discussed.¹³

EXPERIMENTAL

Reagents

Styrene, methyl methacrylate, and sodium *p*-styrene sulfonate (NaSS) were obtained from Wako Pure

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Chemicals Industries Co. The liquid monomers were purified by distillation under reduced pressures shortly before use. Ammonium and potassium persulfates, reagent grade, were purchased from Koso Chemicals Co. The ferrofluid used is Ferricolloid W-35 (magnetite content: 35%) obtained from Taiho Industries Co., Tokyo. Fluorescent dyes, FD-1 and FD-2, were gifts from the Nippon Kayaku Co. Takasaki, Gunma, and used without further purification.

Polymerization

Emulsion polymerizations were carried out in pressure glass bottles as reported before¹⁴ but with some modifications. The latex formed was freed from the coagulum by filtration through a filter paper (Toyo Filter Paper No. 2). The detailed procedure will be described in a separate paper.¹⁵

Latex Yield

A small portion (v mL, usually 2.0 mL) of a latex was dried in an oven at 80°C until a constant weight (w g) was obtained. The latex yield (Y %) in this paper is defined as follows:

$$Y = \frac{100w(V/v)}{M + 0.35F} \quad (1)$$

where M and F are the weights of the monomer and the ferrofluid, respectively, and V is the total volume of the latex. Here, an assumption is made that nothing except magnetite particles is incorporated into the latex particles. The incorporation of initiator fragments and fluorescent dyes was neglected, since their weights were very light.

Particle Diameter

The average diameter of latex particles was obtained by transmission electron microscopy, followed by statistical treatment. A JEOL transmission electron microscope, Model JEM-100B, was used.

Thermal Analysis

A small portion of a latex, which does not have free magnetite particles in its aqueous phase, was freeze-dried after dialysis against pure water for 1 week. The powdery particles were further dried under high vacuum at 40°C for 7 h. Then, 5 or 15 mg of the sample was subjected to thermal analysis, using a SINKU-RIKO thermoanalyzer, Model TGD-

5000RH. Unless otherwise stated, the heating conditions were as follows: heating rate, 10°C/min; temperature range, room temperature to 900°C; and flow rate of nitrogen or air, 80 mL/min. Alumina of the same weight as the sample was used as a reference substance.

Magnetite Content

In most cases, the weight percentage of the residue at 900°C in the thermal analysis in nitrogen, based on the dried latex, is defined as the magnetite content, assuming that the residue is pure magnetite.

RESULTS

Preparation of Magnetic Latex Particles

Emulsion polymerizations of styrene (St) and methyl methacrylate (MMA) were carried out in the presence of a ferrofluid (Ferricolloid W-35; Fc), using ammonium persulfate (APS) or potassium persulfate (KPS) as an initiator and, mostly, adding no surfactants but those in Fc. In some cases, a comonomer (NaSS) or additives such as the fluorescent dyes and calcium chloride were added. Table I summarizes the representative results of emulsion polymerizations to prepare various types of magnetic latex particles. In addition to the latex particles, the main product, a small amount of a magnetic coagulum, was formed concurrently. Under the given conditions, the magnetite particles in the ferrofluid and the dyes were completely incorporated into the latex particles. In general, the average particle diameter (D) of magnetic poly(St) latex particles was larger than that of magnetic poly(MMA) latex particles. Attempts to prepare the latter with larger D by seed polymerization in the presence of Fc were unsuccessful. However, ordinary seed polymerization could conveniently be applied to the preparation of latex particles having functional groups in the cross-linked coating layer (run no. 4).

Figure 1 illustrates the effect of the weight ratio of Fc to St, x_w , on the latex yield, coagulum yield, and particle diameter. The most remarkable feature of these results is that the addition of a small amount of Fc drastically decreased the latex yield. Then, however, it gradually increased with increase in x_w . On the other hand, the particle diameter decreased monotonously with x_w , which would be attributed to the effect of the surfactants in Fc. In line with this, the formation of the coagulum decreased with increase in x_w , except the region of low x_w values,

Table I Preparation of Magnetic Latices of Various Types^a

No.	Monomer (g)	Comonomer (mg)	Fc (g)	Additive (mg)	Initiator (mg)	Yield		<i>D</i> (Å)				
						Coagulum (g)	Latex (%)					
1	MMA	12	—	—	2.4	SDBS	3.75	APS	6	0.073	59.0	600
2	MMA	12	—	—	2.4	—	—	APS	6	0.071	83.2	600
3	MMA	12	—	—	4.8	—	—	APS	6	0.086	52.3	600
4	Seed polymerization ^b using no.1									0.064	82.0	1580
5	St	2	—	—	0.8	—	—	KPS	4	n.d.	55.7	1230
6	St	6	NaSS	60	2.4	—	—	KPS	6	0.051	79.8	1040
7	St	6	NaSS	60	2.4	FD-1	18.0	KPS	6	0.075	50.7	1410
8	St	6	NaSS	60	2.4	FD-2	18.0	KPS	6	0.041	61.6	4360
9	St	6	NaSS	60	2.4	CaCl ₂	16.2	KPS	6	0.049	100	1630

^a Common reaction conditions: total volume, 60 or 20 mL (for run no. 5 only); polymerization temperature, 70°C; polymerization time, 20 h.

^b Reaction conditions: MMA, 1.375 g; methacrylic acid, 0.24 g; 2-hydroxyethyl methacrylate, 0.72 g; ethylene glycol dimethacrylate, 0.0725 g; no. 1, 2%, 20 mL; SDBS, 7.5 mg; APS, 6.0 mg; polymerization temperature, 70°C; polymerization time, 20 h.

presumably owing to the stabilization of the latex by the surfactants in the ferrofluid. The unusual polymerization behavior at low x_w values will be discussed in a separate paper.¹⁵

Basic Study for Thermal Analysis

According to the manufacturer, the ferrofluid used is prepared by the method of Shimoiizaka et al.¹¹ and has colloidal magnetite particles, the surface of which is first coated with sodium oleate and then

with sodium dodecylbenzenesulfonate (SDBS), in an aqueous phase containing SDBS and antifreezing agents. It was concentrated first by evaporation of water and then by drying under high vacuum at 40°C until practically no weight loss was observed. The semisolid residue was subjected to the TG-DTA analysis under nitrogen atmosphere. Figure 2(a) presents the results. The TG curve cannot be elucidated fully, but at least four steps of weight decrease were detected. Most of the organic materials had been removed even under nitrogen atmosphere

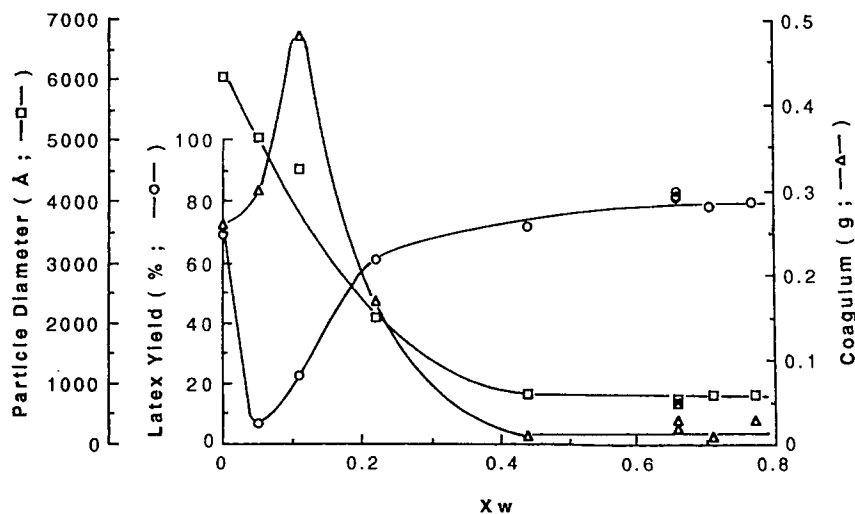


Figure 1 Effect of the weight ratio of the Fc to St (x_w) on the formation of magnetic poly(St) latex particles. Polymerization conditions: St, 6.0 mL; KPS, 12 mg; total volume, 60 mL; temperature, 70°C; reaction time, 20 h.

by the time 900°C was reached. No further decrease of weight was observed up to 1300°C and the weight percentage of the residue was 59.4%. The two-stage decrease of weight with maximum rates at 660 and 730°C is especially characteristic of the ferrofluid.

Figure 2(b) depicts the TG-DTA curves for the concentrated Fc in air under the same conditions as above. Almost no significant weight decrease was observed above 700°C. The two-stage weight decrease is not distinct in this case. When the heating was stopped at 900°C, the residue was dark reddish brown and amounted to 71.8%. The ratio of the residue weight in air to that in nitrogen was 1.21. When heating in air was continued up to 1300°C, there was a gradual slight decrease of weight, and the weight ratio of the residues was 1.17.

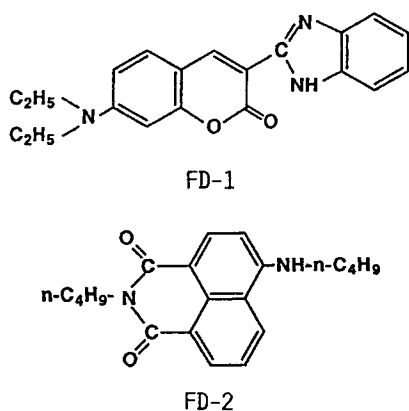


Figure 3(a) and (b) show the TG-DTA data under nitrogen atmosphere for fluorescent dyes FD-1 and FD-2, respectively. The sharp endothermic absorptions of the DTA curves at 244°C (Lit.¹⁶ 214°C) for FD-1 and 132°C (Lit.¹⁶ 125°C) for FD-2 represent the melting points of the dyes. FD-2 was completely decomposed by heating up to 900°C. On the other hand, the decomposition product of FD-1 was so thermally stable that the black residue amounted to 13.5% even at 1300°C, the residue weight still being gradually decreasing. However, the dyes left practically no residue when heated up to 900°C in air in a similar manner. Thus, although both dyes could be incorporated into magnetic latex particles, use of FD-2 is more desirable from the viewpoint of accurate determination of magnetite content.

Magnetite Content in Latex Particles

(A) General Study

It is a prerequisite for accurate and meaningful determination of magnetite content in a latex sample to confirm that no free magnetite particles exist in the aqueous phase of the latex. Thus, this was first

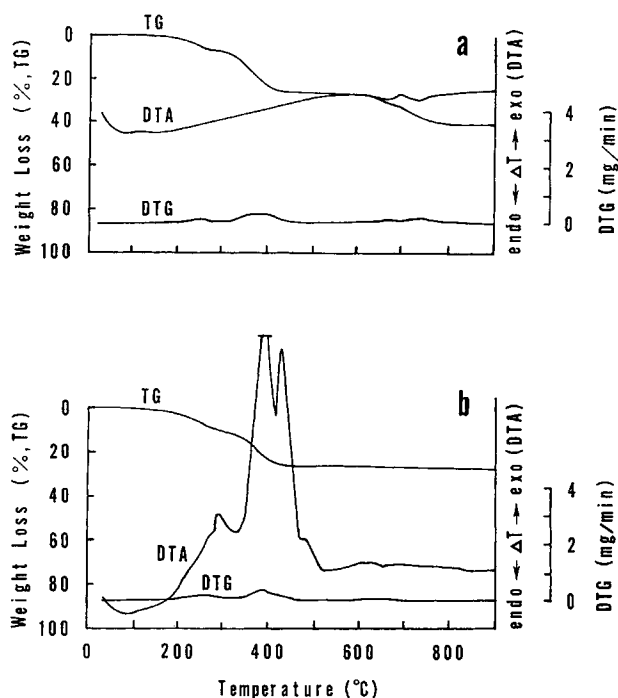


Figure 2 Thermal analysis data for the concentrated ferrofluid taken (a) in nitrogen and (b) in air. Sample weight: 15.3 mg.

done by taking the transmission electron micrographs (TEM) of all the latices, the details of which will be reported in a separate paper.¹⁵ All the dried latex samples were then heated up to 900°C. Reproducibility of the analytical data was sufficiently high. The sample weight should be 5–15 mg, when a semimicro balance is used. However, to ensure high accuracy, more than 10 mg of sample are needed. Table II presents the relevant data of quantitative analysis of magnetite in the latex particles prepared as in Table I.

Figure 4(a) presents the TG-DTA data obtained under nitrogen atmosphere, for a typical dried magnetic poly(St) latex sample with a magnetite content of 11.9%. Starting at ca. 170°C, it decomposed most rapidly at ca. 450°C, which is attributed primarily to the decomposition of poly(St) to St and others.¹⁷ Then, the TG curve suddenly leveled off, followed by a two-stage gradual decrease of weight with maximum rates at ca. 750°C and ca. 800°C. Comparison of the two-stage decrease at temperatures over 700°C with the TG curve of the concentrated ferrofluid [Fig. 2(a)] with maximum rates at 660 and 730°C suggested that, although the temperatures of the two-stage decompositions are considerably different with the two samples, the materials decomposed at these high temperatures were originally from the ferrofluid.

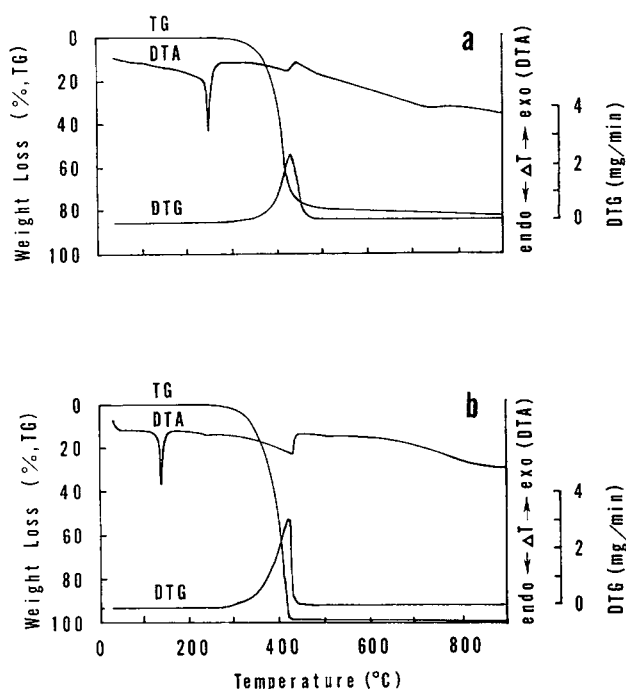


Figure 3 Thermal analysis data for (a) FD-1 and (b) FD-2 in nitrogen atmosphere. Sample weight: 15.3 mg.

Figure 4(b) shows similar data for the same sample decomposed in air, the sensitivity of DTA being half that for the other samples in Figures 2–4. In this case, the two-stage weight decrease at temperatures over 700°C was not observed any more, indicating that, in agreement with the result in Figure 2(b), the materials from the ferrofluid were decomposed at lower temperatures. The two-stage weight decrease was also observed with other types of latex particles pyrolyzed in nitrogen, as shown, for ex-

ample, in Figure 4(c) for a dried magnetic poly(MMA) latex sample (run no. 1 in Table I), which further supports the above inference.

When heated up to 900°C, the residue in air was usually heavier than that in nitrogen atmosphere. The weight ratio of these two residues for the same sample varied in the range of approximately 1.24–1.40, which is considerably higher than the theoretical increase for the oxidation of Fe_3O_4 to Fe_2O_3 (see below). Thus, from a practical point of view, we estimated the magnetite contents of our samples based on poly(St) and poly(MMA) as the weight percentage of the residue at 900°C under nitrogen atmosphere.

However, when the sample was cross-linked, the dried latex sample resisted thermal decomposition in nitrogen. Therefore, the residue in nitrogen was exceptionally heavier than that in air, as was observed in the case of run no. 4 in Table II. In such a case, the residue weight after pyrolysis in air is more reliable. In fact, the magnetite content of the particular latex sample determined in air is much closer to the expected value of 0.8% than that determined in nitrogen. Here, the expected value was calculated with use of the magnetite content of the seed and the particle diameters of the seed and the product, premising that the density of the cross-linked layer is the same as that of poly(MMA).

(B) Magnetic Polystyrene Latex Particles

The analytical method as mentioned above has been applied to a systematic study of the emulsion polymerization of styrene in the presence of the ferrofluid.¹⁵ Part of the results will be discussed here.

Table II Magnetite Contents in the Dried Latex Samples of Various Types Prepared as in Table I^a

No.	N ₂ [15.3 mg]	Air	
		[15.3 mg]	[4.9 mg]
1	13.0	17.2 (1.32)	17.3 (1.33)
2	9.0	—	12.6 (1.40)
3	9.0	—	12.6 (1.40)
4	4.0, 3.9	0.4 (0.10)	—
5	8.5	10.9 (1.28)	10.8 (1.27), 11.0 (1.29), 10.8
6	12.3	15.6 (1.27), 15.7 (1.28)	15.9 (1.29), 16.1 (1.31)
7	12.5	15.0 (1.20)	—
8	11.9	—	15.0 (1.26), 15.3 (1.29), 15.0
9	10.0	—	12.4 (1.24), 12.4

^a The amount of the sample used for the thermal analysis and the ratio of (residue weight in air)/(residue weight in N₂) are given in brackets and parentheses, respectively. The sample numbers are common to both Tables I and II.

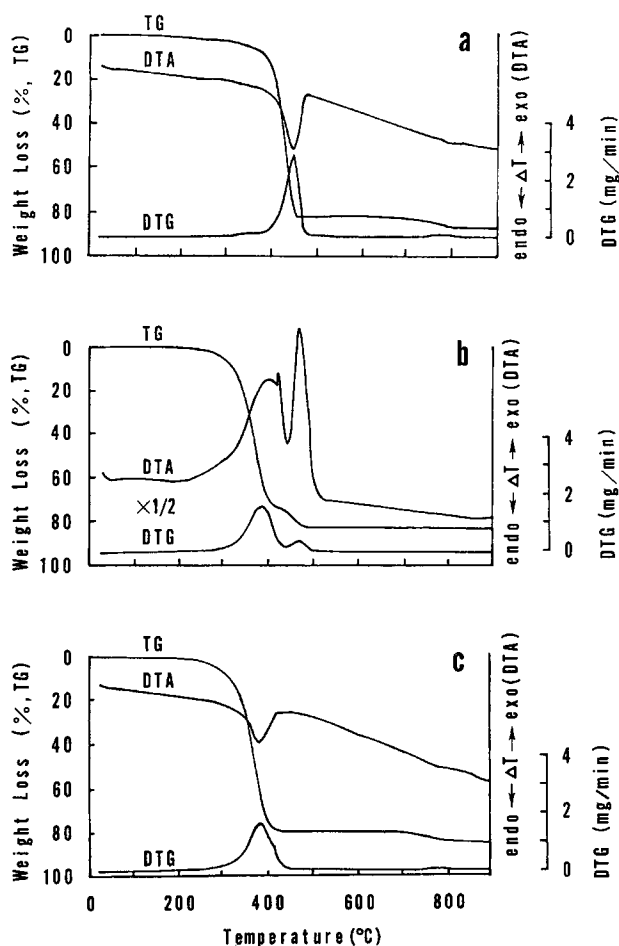


Figure 4 Thermal analysis data for (a) a typical magnetic poly(St) latex sample (magnetite content: 11.9%) in nitrogen, (b) the same sample in air, and (c) a typical magnetic poly(MMA) sample (magnetite content: 13.0%) in nitrogen. Sample weight: 15.3 mg.

Figure 5 shows the magnetite contents of the latex samples prepared as in Figure 1 by filled circles as a function of x_w . In general, the magnetite content increased with increase in x_w . The TEM observation revealed that up to an x_w value of 0.77 no free magnetite particles existed in the aqueous medium of the latex, whereas at $x_w = 0.84$ and 0.88, part of the magnetite particles could not be incorporated into the latex particles.

Comparison of Figure 5 with Figure 1 leads to the conclusion that, when the ferrofluid is used as such, it is difficult to prepare poly(St) latex particles with large diameters containing a large quantity of magnetite in high yield. The maximum magnetite content was 20.8% at $x_w = 0.72$, where the particle diameter was only 670 Å.

Figure 6 discloses that, when the x_w values were low, the DTA and derivative thermogravimetry

(DTG) traces of dried latex samples were also unusual (compare Fig. 6 with Fig. 1). The major endothermic peak of the DTA curve is common to all the samples, irrespective of the x_w values, whereas the minor endothermic peaks appeared at lower temperatures only when x_w was 0.055 and 0.11. The former is due primarily to the thermal decomposition of poly(St).¹⁷ In general, it appeared at higher temperatures with increase in the x_w value. This may suggest that the molecular weight of the polymer increased with x_w owing to the increase of the amount of the surfactants in the emulsion polymerization mixture.¹⁸

DISCUSSION

Determination of Magnetite Content by Thermal Analysis

The present work has established that the magnetite content in magnetic polymeric microspheres can be conveniently determined by thermal analysis (TG-DTA) under nitrogen atmosphere, if the polymer is thermally decomposed readily. The polymers that meet this requirement include those that are thermally decomposed by scission of the main chain, for example, linear poly(St) and poly(MMA). Incorporation of a fluorescent dye such as FD-1 and FD-2 into the latex particles does not interfere with the

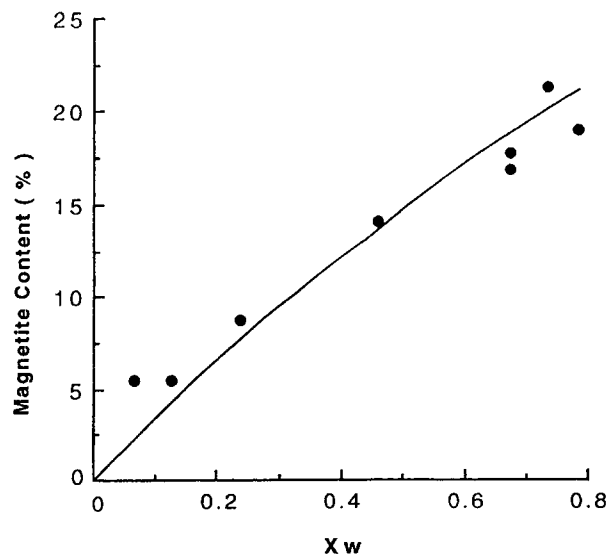


Figure 5 Magnetite contents (filled circles) in dried magnetic poly(St) latex samples prepared at various weight ratios of Fc to St. Polymerization conditions: same as those in Figure 1. The solid curve is for the ideal emulsion polymerization and drawn using eq. (2).

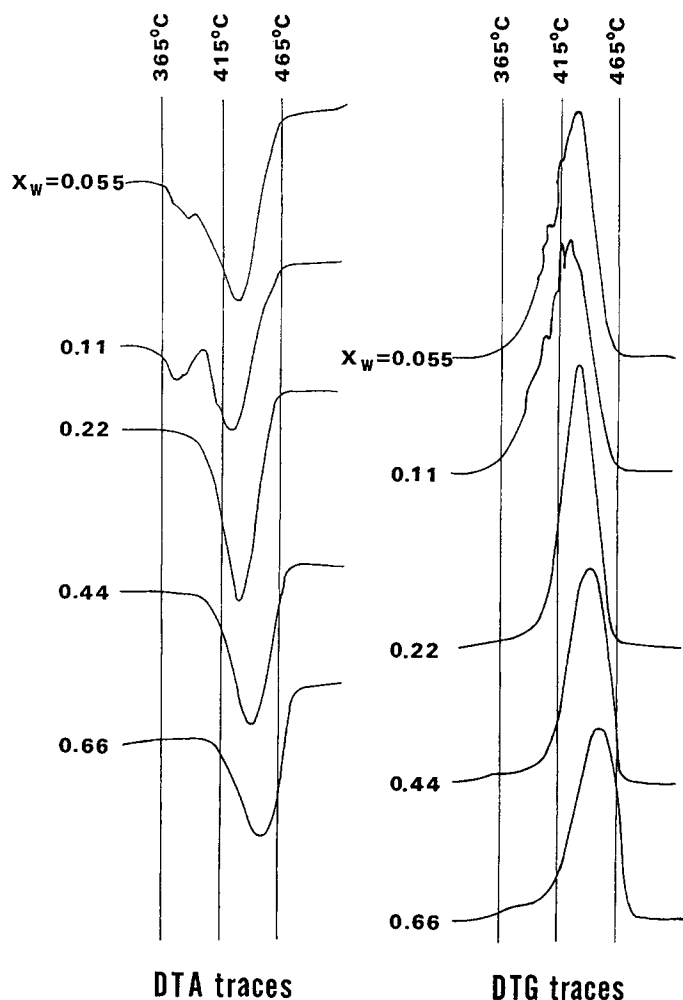


Figure 6 DTA and DTG traces for dried magnetic poly(St) latex samples prepared at various weight ratios of Fc to St (under the same conditions as in Fig. 1).

assay to a significant extent, since the amount of the dye to be used for visualization of the particles through a fluorescence microscope is very small. The method is basically to know the residue weight after the thermal analysis has indicated the completion of the thermal decomposition of the latex particles. Obviously, the morphology of the magnetic polymer does not matter very much.

If the polymeric component is reluctant to thermal decomposition under nitrogen atmosphere, the analysis should be done under an oxygen-containing atmosphere such as air, as exemplified by the magnetic cross-linked polymer (no. 4) in Table II. Thus, the magnetite content can be determined if the organic polymer is completely combustible. However, care should be taken of the possibility that sometimes a violent reaction [see Fig. 4(b)] takes place at about 400°C in air, so that the temperature cannot be controlled.

It should also be noted that the magnetite in Fc is oxidized to α - Fe_2O_3 when heated in air above ca. 400°C. However, when a magnetite-containing sample was heated in air above 600°C, there was a slight decrease of the residue weight. As mentioned earlier, the same phenomenon was observed with the concentrated Fc. These should be due to the dissociation of oxygen from Fe_2O_3 .¹⁹ In fact, when pure Fe_3O_4 was heated up to 1300°C in air, the weight increase by the oxidation was maximum at ca. 550°C and then the weight decreased gradually. At 1300°C, the weight increase was 3.32%, which is slightly smaller than the theoretical increase for the complete oxidation, i.e., 3.46%.

The ratios of the residue weight in air to that in nitrogen were 1.24–1.40 for the latex samples heated up to 900°C (Table II). These are slightly higher than the same values for a few concentrated samples of the ferrofluid itself, i.e., 1.21–1.24 when heated

up to 900°C and 1.14–1.17 when heated up to 1300°C. However, these are considerably higher than the theoretical weight increase, i.e., 1.0346 times, for the oxidation of Fe_3O_4 to Fe_2O_3 . These data suggest that some oxidized organic materials converted from Fc and/or the magnetic latex sample remained even when they were heated up to either 900 or 1300°C in air.

The amount of the magnetic polymer and the heating time required for the present analytical method are only 10–15 mg and less than 1.5 h, respectively. Thus, this method is believed to be more expedient than the ordinary combustion method. Besides, since there is no need to extract iron from the sample, it is more convenient than the colorimetric method^{6b,20} and should be applicable to a wider variety of magnetic polymer samples including cross-linked samples that may not be amenable to the colorimetric method.

Incorporation of Magnetite into Polystyrene Latex Particles

As for the incorporation of magnetite into poly (St) latex particles (Figs. 1 and 5), the percentage magnetite content (W) for the ideal emulsion polymerization, namely, complete conversion of St to latex particles with perfect incorporation of magnetite particles into them, can be correlated with x_w by the following equation:

$$W = \frac{35x_w}{1 + 0.35x_w} \quad (2)$$

taking into consideration that the ferrofluid contains 35% of magnetite and assuming that the organic materials in the aqueous medium of Fc would not be incorporated into the particles and that the coating materials on the surface of magnetite particles is of negligibly small quantity or of the same density as that of poly (St). The solid line for the magnetite content in Figure 5 is based on this equation.

Experimentally, TEM observation of latex particles revealed that perfect incorporation of magnetite particles in them was realized. However, the latex yield was not ideally high at any value of x_w , in particular, at $x_w = 0.05$ – 0.2 . Nevertheless, the experimental magnetite content was considerably close to the curve for the ideal emulsion polymerization. Thus, as far as the emulsion polymerization of St in the presence of the ferrofluid is concerned, the magnetite content is primarily determined by the ratio of Fc to the monomer. However, there is a cer-

tain limit beyond which perfect incorporation of magnetite particles into latex particles cannot be achieved any more. In the present case, this limit is ca. 0.8 in terms of x_w , i.e., ca. 22% as magnetite content according to eq. (2) (see Fig. 5).

The above results suggest that formation of the coagulum would not influence the magnetite content to a significant extent. This may further indicate that complete incorporation of magnetite particles into polymerization nuclei would occur at the early stage of emulsion polymerization and, hence, at a given value of x_w , the coagulum, which is subsequently formed, would also contain almost the same amount of magnetite as that of the latex particles.

Synthesis of magnetic latex particles and the polymerization mechanism will be discussed in more detail in a separate paper.¹⁵

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