Preparation of Fine Polymer Particles Containing Metallocene Derivatives

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SYNOPSIS

This article deals with preparations of fine particles of metallocene copolymers by emulsifier-free emulsion polymerization of vinylferrocene (VFc), ferrocenylmethyl methacrylate (FMMA), 1-ferrocenylethyl methacrylate (1-FEMA), 2-ferrocenylethyl methacrylate (2-FEMA), and 1-ruthenocenylethyl methacrylate (1-REMA) with acrylonitrile (AN), styrene (St), and methyl methacrylate (MMA) in water/ethanol medium. As a result, spherical copolymer particles containing metallocene derivatives have been successfully synthesized in the particle size of ca. 120 to 600 nm. The contents of ferrocenyl or ruthenocenyl groups in copolymer particles increased with increasing concentration of charged metallocene derivatives, while the amounts of metallocene derivatives incorporated into particles are much lower than the charged ratio. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A large number of syntheses and properties of fine polymer particles of submicron size have attracted much attension. The typical techniques for the formation of fine polymer particles are as follows; emulsion polymerization with conventional emulsifier, seeded emulsion polymerization, and emulsifier-free emulsion polymerization. The particles formed by emulsifier-free emulsion polymerization are generally highly monodispersed in size and their surfaces are clean without emulsifier.

The syntheses of a variety of fine particles composed of homo- or copolymers by emulsifier-free emulsion polymerization have been carried out.[1] We can readily control the properties of fine polymer particles by copolymerizing monomers containing functional groups such as carboxyl and sulfonate groups, e.g., acrylic acid,[2,3] sodium styrene sulfonate,[4] and acrylamide[5] with conventional monomers. However, there have been a few reports on the synthesis of fine particles consisting of copolymers containing metal or metal ions. Regarding polymer/metal composite particles, fine polymer particles containing ultrafine metal particles such as magnetite and the polymer particles coated with metal by well-known electroless plating technique have been reported.[6-8] The former is a kind of heterogeneous core-shell type particle and in the latter case, only the surface of particle is metallized. However, there have been few reports on the preparation of fine polymer particles in which metal atoms are dispersed uniformly. Metal atoms-dispersed fine polymer particles are expected as functional composite particles having both characteristics of polymer and metal, for instance, as a binder materials between metal and polymer.

On the other hand, it has been reported that a few vinyl organometallic monomers have been homo- and copolymerized by cationic and free radical initiators.[9,10] Arimoto and Haven,[9] Baldwin and Johnson,[10] and Pittman et al.[11] have studied the azobisisobutyronitrile (AIBN)-initiated homopolymerization of vinylferrocene (VFc). Lai et al. reported that ferrocenylmethyl acrylate, and ferrocenylmethyl methacrylate (FMMA) were polymerized in benzene solution using AIBN as initiator.[12] In addition, Pittman et al.[13,14] found that 2-ferrocenylethyl methacrylate (2-FEMA) and 2-ferrocenylethyl acrylate were readily homo- and co-polymerized in benzene solution using AIBN initiator.

From these points of view, in this work, we at-

tempted to introduce metal complexes into fine polymer particles by copolymerization of vinyl organometallics such as vinylferrocene (VFc), FMMA, 1-ferrocenylethyl methacrylate (1-FEMA), 2-FEMA, and 1-ruthenocenylethyl methacrylate (1-REMA) with acrylonitrile (AN), styrene (St), and methyl methacrylate (MMA). Because these vinyl organometallics contain both metallocene group in molecular structure and a polymerizable double bond, Incorporation of metal and metal ions into polymer particles seems possible. The effect of concentration of metallocene containing monomers on the particle formation and on the amounts of metallocene unit incorporated into particles were investigated.

EXPERIMENTAL

Materials

Ferrocene from Wako Pure Chemical Ind. was sublimed before use. Methacryloyl chloride (Aldrich, INC.) and pyridine (Wako Pure Chemical Ind.) were distilled. St, MMA, and AN were distilled under reduced pressure. AIBN (Tokyo Kasei Co.), 2,2-Azobis(2-amidinopropane) hydrochloride (AAP; Wako Pure Chemical Ind.), and potassium persulfate (KPS; Wako Pure Chemical Ind.) used as initiators were recrystallized. Ethyl ether was dried over Na–K alloy and distilled before use. Other chemicals were all analytical grade from Wako Pure Chemical Ind. and were used without further purification. Distilled and deionized water was used throughout the experiments.

FMMA was prepared by esterification of hydroxymethylferrocene[15] derived from N,N-dimethylaminomethylferrocene with methacryloyl chloride.[12] The nmr spectrum (CDCl3) was in accord with the title compound: δ 1.96 (s, 3H, CH$_3$), 4.15 (s, 5H, unsubstituted Cp hydrogens), 4.20 and 4.26 (s, 4H, substituted Cp hydrogens), 4.83 (s, 2H, CH$_2$), 5.56 and 6.13 (s, 2H, vinyl).

1-FEMA was prepared by esterification of 1-hydroxyethylferrocene with methacryloyl chloride.[13] 1-Hydroxyethylferrocene was prepared by reduction of acetylferrocene with sodium borohydride. 1-Hydroxyethylferrocene (1.32×10^{-2} mol) was dissolved in 10 mL of dry ethyl ether and 2.4×10^{-2} mol pyridine was added. The mixture was stirred for 5 min on an ice bath. Then 2.4×10^{-2} mol methacryloyl chloride was added at 0°C. The reaction was conducted for 3 h. The precipitated product was isolated by filtration and washed with sodium bicarbonate aqueous solution, sodium chloride solution, and wa-

ter. 1-FEMA thus obtained was then recrystallized from petroleum ether. NMR (CDCl$_3$) δ 1.96 (s, 3H, CH$_3$), δ 1.54 (d, 3H, J = 6.53 Hz, CH$_3$), 4.14 (s, 5H, unsubstituted Cp hydrogens), 4.19 and 4.25 (s, 4H, substituted Cp hydrogens), 5.85 (q, 1H, J = 6.47 Hz, —CH), 5.55 and 6.12 (s, 2H, vinyl).

1-REMA was prepared in essentially the same method as that for 1-FEMA. The nmr spectrum (CDCl$_3$) was in accord with the title compound: δ 1.94 (s, 3H, CH$_3$), 1.45 (d, 3H, J = 6.53 Hz, CH$_3$), 4.53 (s, 5H, unsubstituted Cp hydrogens), 4.51 and 4.65 (s, 4H, substituted Cp hydrogens), 5.68 (q, 1H, J = 6.47 Hz, CH), 5.54 and 6.08 (s, 2H, vinyl).

2-FEMA was synthesized starting from N,N-dimethylaminoethylferrocene.[13] Nmr (CDCl$_3$): δ 1.95 (s, 3H, CH$_3$), 2.70 (tr, 2H, J = 6.96 Hz, CH$_2$), 4.27 (tr, 2H, J = 6.98 Hz, OCH$_2$), 4.12 (s, 5H, unsubstituted Cp hydrogens), 4.08 and 4.11 (s, 4H, substituted Cp hydrogens), 5.56 and 6.11 (s, 2H, vinyl).

Preparation of Fine Polymer Particles

Preparations of fine copolymer particles were carried out in round bottomed flasks. The contents of the flask were stirred with a Teflon half-moon type stirrer at a speed of 300 rpm. The preparation were exemplified in the following two methods:

Single-Stage Polymerization

AN/VFc Copolymer Particles. Water/ethanol (50 mL, volume ratio 1/1), 0.15 mol of AN and 1.5 $\times 10^{-2}$ mol of VFc (or FMMA) were charged to a round-bottom glass flask and the mixture was stirred at room temperature for 1 h. The mixture was heated up to 70°C and then 3×10^{-4} mol of AIBN was added. The polymerization was allowed to continue at 70°C for 12 h under Ar atmosphere.

St/1-FEMA Copolymer Particles. Water/ethanol (45 mL, volume ratio 7/3), 3.7×10^{-3} mol of St, and 3.7×10^{-4} mol of 1-FEMA were charged to a round-bottom flask and the mixture was heated up to 70°C under stirring. AIBN (2×10^{-5} mol) dissolved in 5 mL of ethanol was added and the polymerization was allowed to continue for 12 h at 70°C under Ar atmosphere.

Seeded Polymerization

AN/St/VFc Copolymer Particles. Water (20 mL), 0.1 mol of St, and 10^{-2} mol of AN were charged to a flask and the mixture was heated up to 70°C under

stirring. The preparation of St/AN copolymer particles was conducted by addition of 2.4×10^{-4} mol of KPS dissolved in 5 mL of water. After 8 h, 10^{-2} mol of VFc dissolved in ethanol (20 mL) and 2×10^{-4} mole of AIBN dissolved in ethanol (5 mL) were added to the dispersion. The polymerization was allowed to continue for 12 h at 70°C.

St/1-FEMA or 2-FEMA and MMA/1-FEMA Copolymer Particles. Water/ethanol (10 mL, volume ratio 7/3), and 10^{-2} mol of MMA (or 2×10^{-2} mol of St) were charged to a flask and the mixture was heated up to 70°C under stirring. 2×10^{-5} mol of AAP was added and after 2 h, the fixed amount of 1-FEMA (or 2-FEMA) dissolved in 40 mL of water/ethanol (volume ratio 7/3) was added to the dispersion of poly(MMA) (or St) particles with 1.28×10^{-4} mol of AIBN. The polymerization was allowed to continue at 70°C for 12 h.

St/1-REMA Copolymer Particles. Water/ethanol (10 mL, volume ratio 7/3) and 0.15 mol of St were charged to a flask and the mixture was heated up to 70°C under stirring. The polymerization of St was conducted by addition of 3×10^{-4} mol of AAP. After 2 h, 1.5×10^{-3} mol of 1-REMA dissolved in 40 mL of water/ethanol (volume ratio 7/3) was added with 3×10^{-4} mol of AIBN. The polymerization was allowed to continue at 70°C for 12 h.

In all preparations of the copolymer particles, the dispersions obtained were centrifuged and the sedimented particles were redispersed in distilled water to remove the unreacted monomers. This procedure was repeated three times and then the particles were filtered through G-1 glass filter to remove any coagula.

Measurements

The average particle sizes were determined by TEM micrographs with Akashi EM-002B. Metal contents in copolymer particles were determined by particle induced X-ray emission (PIXE) analysis. The intensities of characteristic x-ray generated from samples by irradiation of proton accelerated by a van de Graaff accelerator system were measured by X-ray detector. Since the intensities of characteristic x-ray produced were proportional to the metal atom concentrations of samples, the metal contents in particles were calculated using standard metal samples. The contents of metal in particles were calculated using standard metal samples. ^{1}H-NMR spectra were run on a JEOL-JNM-270 spectrometer and recorded downfield in parts per million from tetramethylsilane.

RESULTS AND DISCUSSION

AN/VFc Copolymer Particles

Synthesis of spherical particles of homopolymers containing poly(VFc) and poly(FMMA) has failed in water/ethanol 1 : 1 or 1 : 0 systems since coagula formation is predominant. Therefore, we have attempted the copolymerizations of these monomers with AN, St, and MMA. VFc and AN are soluble in 1 : 1 water/ethanol solution, but VFc is insoluble in water. The effect of VFc concentration on the formation of AN/VFc copolymer particles are shown in Table I. In the case of single stage poly-

Table I Preparation of AN/VFc Copolymer Particles

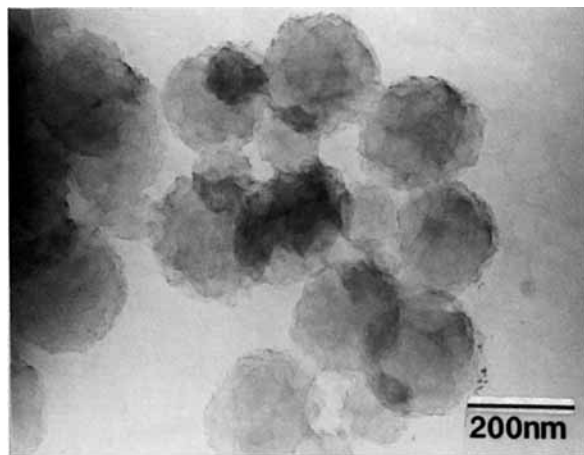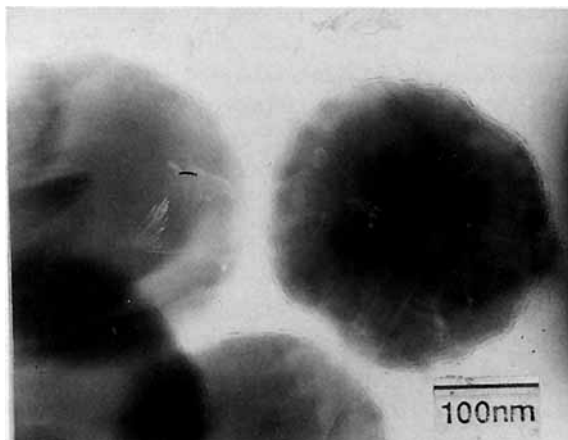|	Monomer Ratio (mole)			Particle Yield (%)	Diameter (nm)	Unit Ratio in Particle (mole)		
	AN	St	VFc			AN	St	VFc
Poly (AN/VFc)	100	—	2.5	83.6	167	100	—	0.18
	100	—	5.0	60.7	122	100	—	0.25
	100	—	10.0	44.8	177	100	—	0.35
Poly (AN/St/VFc)[a]	100	10	2.5	74.3	315	100	24	0.26
	100	10	5.0	80.1	244	100	20	0.41
	100	10	10.0	75.7	201	100	23	0.62

Initiator: AIBN 4.8 mmole/L.
Water/Ethanol = 1/1.
Polymerization: 70°C, 12 h.
[a] Seeded polymerization of poly (AN/St) particles.

merization, the particle yields decreased with increasing concentration of charged VFc. In particular, at high concentration of VFc(AN/VFc mole ratio = 100/10), coagula formation becomes predominant and the yield of spherical particle is only 44.8%. The charged AN/VFc ratio is limited to 100/2.5 for high conversion of particles. In general, the fine particles formed by emulsifier-free emulsion polymerization in water are stabilized by electrostatic repulsion between particles and additionally steric repulsion due to adsorbed polymer if water-soluble polymer was used as stabilizer. The electrostatic repulsion is dependent on the surface potential derived from surface charge, and surface charge of fine polymer particles arises from the dissociation of ionic groups on the surface. If persulfate such as KPS and AAP are used as initiator, decomposed components of these initiators, most of which are combined to the ends of polymer chains, give ionic groups on the surface of polymer particles. However, AIBN used in the preparation of AN/VFc copolymer particles gives no ionic group to the end of polymer chain, and hence the surface charge of AN/VFc copolymer particles is low to result in weak electrostatic repulsion between particles. The AN/VFc copolymer particles obtained were spherical as shown in TEM photographs in Figure 1. The average particle diameters range from ca. 120 nm to 180 nm. These particle sizes were lower as compared with those of poly(St) particles produced by single stage emulsifier-free emulsion polymerization in water using KPS. The smaller particle sizes of AN/VFc copolymer particles may be attributed to the production

Figure 2 Transmission electron micrograph of poly(AN/FMMA) fine particles.

of a large number of nuclei in the nucleation stage. The contents of VFc incorporated in particles, which were calculated from Fe content determined by PIXE analysis, increased with increasing concentration of charged VFc, but the upper limit of incorporated VFc is only 0.35%.

In order to increase particle yield, seeded polymerization of VFc was attempted using St/AN copolymer as seed particles. As shown in Table 1, the particle yields and the contents of VFc incorporated indicate the higher values (0.62%) than those by single stage polymerization. However the amounts of VFc incorporated are still lower than charged one. This is reasonable to the low solubility of VFc in water/ethanol and the low monomer reactivity of VFc.

AN/FMMA Copolymer Particles

The use of FMMA in place of VFc should result in the formation of particles containing FMMA unit in high concentration since FMMA exhibits higher monomer reactivity than VFc. FMMA is soluble in a 1 : 1 water/ethanol solution. The TEM photograph of the particles obtained is shown in Figure 2. The particles are spherical. The average sizes and the compositions of AN/FMMA copolymer fine particles obtained are shown in Table II. In fact, the content of ferrocenyl group in particles reaches 2.4% of AN, about five times higher than that of VFc. On the copolymerization of FMMA with St, MMA and vinylacetate (VAc), Pittman et al.[12] found that FMMA was copolymerized to low conversion with St and MMA in benzene at 70°C, while FMMA was

Figure 1 Transmission electron micrograph of poly(AN/VFc) fine particles obtained by single-stage polymerization.

Table II Preparation of AN/FMMA Copolymer Particles

Monomer Ratio (mole)		Particle Yield (%)	Diameter (nm)	Unit Ratio in Particle (mole)	
AN	FMMA			AN	FMMA
100	10	66	168	100	1.9
100	20	51	181	100	2.4

Initiator: AIBN 4.8 mmole/L.
Polymerization: 70°C, 12 h.
Water/Ethanol = 1/1.

copolymerized to higher conversion with VAc. They reported that the reactivity ratios were $r_1 = 0.03$ and $r_2 = 3.7$ for St (M_2), $r_1 = 0.12$ and $r_2 = 3.27$ for MMA (M_2), and $r_1 = 1.52$ and $r_2 = 0.2$ for VAc (M_2), and attributed the low conversions of FMMA with St to the small magnitude of r_1. Similarly, the low content of FMMA in the copolymer particles of FMMA with AN in this work is speculated to be due to a small value of r_1 for FMMA.

St/1-FEMA or 2-FEMA and MMA/1-FEMA Copolymer Particles

St and vinyl organometallics used here have low solubility in water and the formation of spherical particles occurred readily by emulsifier-free polymerization. The solubilities of St and vinyl organometallics can be adjusted by using a suitable cosolvent such as alcohol because of their miscibility with both water and these monomers. On the effect of alcohol,

Table III Polymerization of Styrene in Water–Ethanol

Water : Ethanol	Conc. of St (mol/l)	Yield (%)	Diameter (nm)	Mn
9 : 1	0.1	—[a]	—	—
	0.2	67	350	84000
	0.4	24	400	65000
7 : 3	0.2	—[a]	—	—
	0.4	59	400	93000
	0.6	32	500	71000
1 : 1	0.4	—[a]	—	—
	0.6	37	300	54000
	0.8	12	500	68000

Initiator; AAP 4 mmol/L; polymerization; 70°C, 14 h.
[a] No particles.

Table IV Polymerization of MMA in Water–Ethanol

Water : Ethanol	Conc. of MMA (mol/l)	Yield (%)	Diameter (nm)	Mn
9 : 1	0.1	—[a]	—	—
	0.2	72	350	88000
	0.3	12	400	79000
7 : 3	0.1	—[a]	—	—
	0.2	65	450	106000
	0.3	32	400	69000
1 : 1	0.2	41	500	74000
	0.3	26	650	81000
	0.5	18	600	86000

Initiator; AAP 4 mmole/L; polymerization; 70°C, 14 h.
[a] No particles.

Homola et al.[16] studied the emulsifier-free emulsion polymerizations of St in the presence of methanol, and found that the increase in methanol concentration resulted in reduction of the particle size instead particle yield was much improved. Chonde and Krieger[17] investigated the effect of methanol on the copolymerization of sodium vinylbenzyl sulfonate with styrene and found that particle size increased with increasing methanol content.

On the basis of these facts, we investigated first the effect of ethanol concentration on the formation of St and MMA homopolymer particles, prior to the examination to form St/1-FEMA or 2-FEMA and MMA/1-FEMA copolymer particles. The results are shown in Tables III and IV), respectively, for St and MMA. The particle yield decreased with increasing ethanol, and St or MMA concentration. In general, the potential of solid surface in nonaqueous solvent is lower than that in water and the electrostatic repulsion between particles is weak. Thus, the high ethanol content lowers the colloidal stability of polymer particles and causes the coagulation of particles. In fact, in the case of low concentrations of St such as 0.1, 0.2, or 0.4 mole/L for water/ethanol ratio of 9/1, 7/3, and 1/1, respectively, no particle was formed. Accordingly, as shown in Table 3, optimum concentrations to precipitate the fine particles of poly(St) was found to be 0.2 mol/L, 0.4 mol/L, and 0.6 mol/L, respectively, for 9/1, 7/3, and 1/1 water/ethanol ratio. Ethanol concentration has no influence on both particle size and molecular weight of polymer as shown in Tables III and IV. On the other hand, 10^{-2} mole of 1-FEMA was found to be soluble in water/ethanol system (7 : 3).

Based on these results, we performed the syn-

Table V Preparation of St or MMA/FEMA Copolymer Particles

|	Monomer Ratio (mol)				Particle Yield (%)	Diameter (nm)	Unit Ratio in Particle (mol)			
	St	MMA	1-FEMA	2-FEMA			St	MMA	1-FEMA	2-FEMA
Poly (St/1-FEMA)	100	—	10	—	46	455	100	—	0.3	—
	100	—	20	—	37	513	100	—	1.1	—
Poly (St/1-FEMA)[a]	100	—	5	—	58	539	100	—	1.1	—
	100	—	10	—	43	549	100	—	1.8	—
Poly (MMA/1-FEMA)[a]	—	100	5	—	49	519	—	100	0.7	—
	—	100	10	—	46	406	—	100	1.6	—
Poly (St/2-FEMA)[a]	100	—	—	5	57	536	100	—	—	1.5
	100	—	—	10	39	553	100	—	—	2.3

Initiator: AIBM 4.8 mmole/L.
Polymerization: 70°C, 12 h.
Water/Ethanol = 7/3.
[a] Seeded polymerization.

thesis of St/1-FEMA copolymer particles in water/ethanol = 7/3 using AIBN as initiator. The results are shown in Table V. Although the yield of copolymer particles formed by single stage polymerization decreased with increase of charged 1-FEMA, the amounts of 1-FEMA incorporated into particles increased up to St/1-FEMA = 1/1 $\times$ 10^{-2} mole ratio in case of water/ethanol 7/3 ratio. Figure 3 shows the TEM photograph of the particles obtained by single-stage polymerization. In sharp contrast to this system, the coagulation occurred preferentially in the case of water/ethanol 1 : 1 ratio. As described above, this is attributed to the low colloidal stability of particles at high ethanol concentration. In order to obtain colloidally stable polymer particles containing higher content of 1-FEMA, seeded polymerization was tested starting from poly (St) and poly (MMA) seed particles. After prepolymerization of St or MMA, 1-FEMA or 2-FEMA were added to the polymerization systems. The results are shown in Table V. Figure 4 shows the TEM photograph of the particles obtained here. The amounts of incorporated 1-FEMA and 2-FEMA units increased with increasing charged FEMA. The ratios of 1-FEMA copolymerized with MMA are slightly lower than that with St. The monomer reactivity ratios were reported to be 2-FEMA-St r_1 = 0.08, r_2 = 0.58; 2-FEMA-VAc r_1 = 8.79, r_2 = 0.06; 2-FEMA-MMA r_1
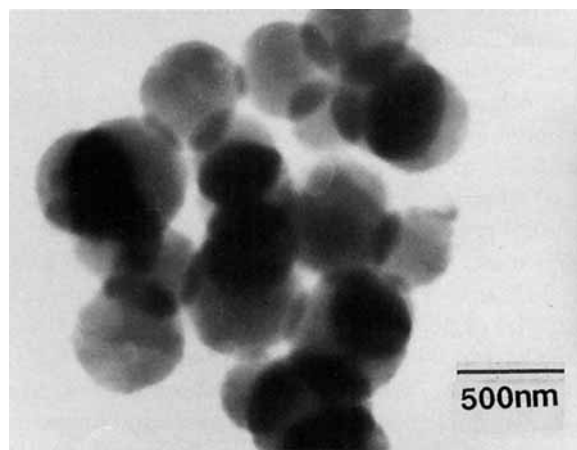
Figure 3 Transmission electron micrograph of poly (St/1-FEMA) fine particles obtained by single-stage polymerization.
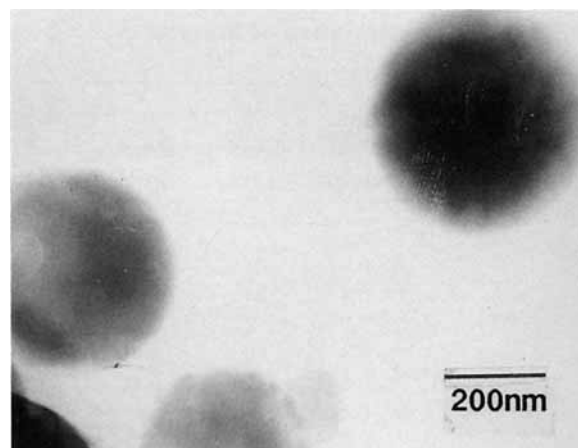
Figure 4 Transmission electron micrograph of poly (St/2-FEMA) fine particles obtained by seeded polymerization.

= 0.20, r_2 = 0.65.[14] These results indicate that 2-FEMA is more reactive than FMMA. However, the amounts of 2-FEMA incorporated into the copolymer particles in this work were generally lower than those of FMMA. This conflict may arize from the solution property consisting of water and ethanol.

In order to stabilize the particles, we attempted to increase the surface charge by treating St/1-FEMA copolymer particles with H_2SO_4 and NH_4PF_6.[18] These system brings about the change of ferrocenyl group to Fe(III) (ferrocenyl cation). After treatment, highly colloidally stable dispersion of 1-FEMA/St copolymer particles were obtained. The electrostatic repulsion due to ferrocenylcations seems to stabilize the particles.

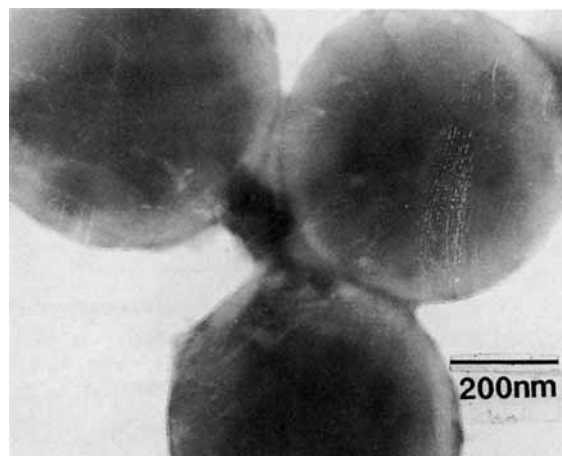## St/1-REMA Copolymer Particles

We also attempted to synthesize fine polymer particles containing ruthenocene by single-stage emulsifier-free emulsion copolymerization of 1-REMA and St in water/ethanol mixture using AIBN as initiator. However, colloidally stable spherical polymer particles did not form by single stage copolymerization. SEM observation of polymer particles indicated the formation of aggregates of fine particles. Seeded polymerization using poly(St) fine particles as seed particles was utilized for the synthesis of St/1-REMA copolymer particles. The results of the seeded polymerization are shown in Table VI. As shown in TEM photographs in Figure 5, St/1-REMA copolymer particles are spherical. Their particle sizes range from 600 nm to 700 nm and these are monodispersed. The particle yields slightly decreased with increasing concentration of 1-REMA. Similarly to St/1-FEMA particles prepared by seeded polymerization, the incorporation of ruthenocenyl group into particles is supposed to lower

Figure 5 Transmission electron micrograph of poly(St/1-REMA) fine particles.

the colloidal stability of copolymer particles. The amounts of 1-REMA incorporated into copolymer particles (3.0 mol % of St) determined by ^{1}H-NMR spectrum increased with increasing charged 1-REMA.

In order to obtain fine polymer particles containing high amounts of metal atoms uniformly in particles, the preparation of fine polymer particles by copolymerizing vinyl metallocene derivatives was attempted. However, the incorporation of metallocene into particles was not stoichiometry though a small amount of metallocene was incorporated. In future, the stoichiometric incorporation of vinyl organometallics should be investigated.

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Table VI Preparation of St/1-REMA Copolymer Particles

Monomer Ratio (mole)		Particle Yield (%)	Particle Diameter (nm)	Unit Ratio in Particle (mol)	
St	1-REMA			St	1-REMA[a]
0.1	0.002	57	700	100	1.5
0.1	0.005	43	590	100	3.0
0.1	0.01	41	690	100	3.0

Initiator; AIBN 4 mmole/L; polymerization; 70°C, 10 h; Solvent; Water : Ethanol = 7 : 3.

[a] Determined from ^{1}H NMR spectra.

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