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Preparation of Polymer-Protected Colloidal Dispersions of Copper

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Colloidal copper dispersions are prepared by reducing copper(II) ions in water with sodium tetrahydroborate or hydrazine in the presence of various protective polymers. The polymers are poly(*N*-vinyl-2-pyrrolidone), poly(vinyl alcohol), poly(methyl vinyl ether), poly(potassium vinyl sulfate), dextrin, amylopectin, methylamylopectin, methylcellulose, ethylcellulose, and (2-hydroxyethyl)cellulose. The dispersions are black, reddish dark brown, or reddish brown homogeneous solutions, and are stable under nitrogen at room temperature for more than three months. Electron diffraction experiments indicate that copper atoms in the colloidal particles are arranged in an ordered way, which is almost identical with that in a crystal of bulk copper metal. At the charged molar ratio 40 of the monomeric residue of the protective polymer to copper(II) ion, the average diameters of the copper particles, prepared by use of sodium tetrahydroborate, range from 50 to 150 Å, depending on the polymer used. With the use of poly(*N*-vinyl-2-pyrrolidone) as protective polymer, the size of the copper particles monotonously increases with increase in the degree of polymerization of the polymer and also with decrease in the amount of the polymer.

Colloidal dispersions of noble metals such as rhodium, ruthenium, and platinum were prepared by reduction of the corresponding metal salts in the presence of protective polymers, using molecular hydrogen,[1,2] hydrazine,[3] formaldehyde,[4] sodium tetrahydroborate,[5] and alcohols[6–9] as reducing agents. These dispersions exhibited high and selective catalytic activities in hydrogenation of olefins and nitro groups. However, information on the preparation of colloidal dispersions of non-noble metals and their properties has been rather scant.

Papavassiliou and Kokkinakis[10] prepared a colloidal copper dispersion by reducing copper(II) sulfate with hydrazine in the presence of gelatin. However, concurrent precipitation took place in the reduction, and homogeneous solution was obtained only after the removal of large particles of copper by centrifugation. No information on the size of copper particles was presented there.

In a preliminary communication,[11] the authors reported that homogeneous colloidal dispersions of copper could be prepared by reducing copper(II) sulfate with sodium tetrahydroborate in the presence of poly(*N*-vinyl-2-pyrrolidone) or poly(vinyl alcohol). The resulting colloidal dispersions were highly active and selective in the hydration of acrylonitrile to acrylamide.

This paper will report preparation of colloidal copper dispersions using various kinds of protective polymers, copper salts, and reducing agents. Results of electron microscopy on the colloidal particles will be described. Furthermore, effects of degree of polymerization of protective polymers and their amounts on the size of colloidal particles will be shown.

Experimental

Materials. Poly(*N*-vinyl-2-pyrrolidone)s, amylopectin, methylcellulose (degree of methylation, 2.0), (2-hydroxyethyl)cellulose (degree of hydroxyethylation, 1.6) (from Tokyo Kasei Kogyo Co.), poly(vinyl alcohol)s (from Pure Chemicals Co.), dextrin (from Kanto Chemicals), and ethylcellulose (degree of ethylation, 1.0, from Nakarai Chemicals) were repeatedly (2—5 time) reprecipitated from aqueous solutions with the addition of acetone. Poly(potassium vinyl sulfate), β-cyclodextrin (from Nakarai Chemicals), poly(methyl vinyl ether) (from Tokyo Kasei Kogyo Co.), poly(acrylic acid), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (from Aldrich Chemical Co.), and a copolymer of methyl vinyl ether and maleic acid (methyl vinyl ether composition 0.62, from Scientific Polymer Products) were used without further purification. Soluble nylon, in which 30% of the hydrogens in the α-methylene groups with respect to the carbonyl groups in nylon 6 were substituted with diethylamino groups, was kindly provided by Toray Chemical Co. Poly(aminoethylene)[12] and methylamylopectin[13] were prepared according to the literatures. The degree of methylation with respect to glucose unit in the methylamylopectin was 1.1 as determined by ^{1}H-NMR spectroscopy.

Copper(II) sulfate from Yoneyama Chemical Co. was recrystallized three times from aqueous solution. Copper(II) chloride, copper(II) nitrate, and copper(II) acetate were obtained from Koso Chemical Co. Doubly distilled water was degassed by boiling under a reduced pressure.

Sodium tetrahydroborate (Koso Chemical Co.) was stored over silica gel and was dissolved in water immediately before use. Hydrazine hydrate and aqueous formaldehyde solution (37 wt%) were obtained from Nakarai Chemicals and Yoneyama Chemical Co., respectively. Nitrogen gas and hydrogen gas, which had purities higher than 99.9995 and 99.999%, respectively, were purchased from Nippon Sanso Co.

Preparation of Colloidal Copper Dispersion. Copper salts and various amounts of polymers were dissolved in water, and were stirred magnetically at 80 °C under nitrogen for 1 h. The stirring was made at 25 °C instead of 80 °C only for the case of poly(methyl vinyl ether), since this polymer dissolved in water at 25 °C but not at 80 °C. Then, aqueous solution of sodium tetrahydroborate, hydrazine, or formaldehyde was added to the resulting solution at 25 °C. Reduction using molecular hydrogen was carried out at 80 °C for 20 h under hydrogen pressure 37 atm.

Preparation with the use of methanol containing alkali as reducing agent was carried out as follows. Copper salts and

Table 1. Preparation of Colloidal Copper Dispersions by Reduction of Copper(II) Sulfate with Sodium Tetrahydroborate in the Presence of Various Polymers[a)]

Polymer	Degree of polymerization	Colloid	
		Color	Average particle diameter/Å
Poly(*N*-vinyl-2-pyrrolidone)	6300		b)
	3240		100
	1440	Reddish dark brown	60
	360		b)
	90		50
Poly(vinyl alcohol)	2000		b)
	1500		150
	360		b)
Poly(methyl vinyl ether)	570		b)
Poly(potassium vinyl sulfate)	b)	Black	b)
Dextrin	b)		90
Amylopectin	b)		100
Methylamylopectin	b)		b)
Methylcellulose	140		100
Ethylcellulose	b)	Reddish dark brown	b)
(2-Hydroxyethyl)cellulose	b)		b)

a) $[CuSO_4]_0=5.0\times10^{-3}$ mol dm^{-3}; [monomeric residue of protective polymer]$_0=2.0\times10^{-1}$ mol dm^{-3}; $[NaBH_4]_0=1.0\times10^{-2}$ mol dm^{-3}; Suffix 0 refers to the charged concentration. b) Not determined.

polymers were dissolved in 1: 1 methanol–water mixture, and the solutions were stirred magnetically at 80 °C for 1 h, and then aqueous solution of sodium hydroxide was added. The solution was further kept at 80 °C for 10 min.

Electron Microscopy. Electron micrographs of the colloids were measured on a Hitachi Model HU-12A electron microscope operated at 100 kV. Sample films were prepared under nitrogen from the colloidal dispersions on collodion films coated with a carbon layer, by evaporating the solvent to dryness.

Absorption Spectroscopy. Absorption spectra of the colloidal dispersions were taken under nitrogen on a Hitachi Model 340 spectrometer at 25 °C using 1 cm quartz cell.

Results

Preparation of Colloidal Copper Dispersions Using Sodium Tetrahydroborate as Reducing Agent. As shown in Table 1, homogeneous colloidal copper dispersions were successfully prepared by reducing copper(II) sulfate with sodium tetrahydroborate in the presence of various polymers as protective polymers. The protective polymers were poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(vinyl alcohol), poly(methyl vinyl ether), poly(potassium vinyl sulfate), dextrin, amylopectin, methylamylopectin, methylcellulose, ethylcellulose, and (2-hydroxyethyl)cellulose. Here, the charged molar ratio of monomeric residue of the polymer to copper(II) sulfate was kept constant at 40.

The resulting colloidal copper dispersions were highly stable under nitrogen. For example, neither change in color nor precipitation was detected, when the colloidal dispersion with PVP of viscosity-averaged degree of polymerization (DP) 3240 was kept under nitrogen at room temperature for more than three months. On contacts with oxygen, however, the dispersions turned into yellow in a few minutes.

Stable colloidal copper dispersion was obtained even at the charged molar ratio 5 of monomeric residue of PVP (DP=3240) to copper(II) sulfate. At the charged molar ratio 1.0, however, the dispersion was less stable and considerable amounts of black precipitates were formed in 1 h.

In contrast with the formation of homogeneous colloidal dispersions in the presence of these protective polymers, black precipitates were rapidly formed in their absence. The precipitation took place immediately after the addition of sodium tetrahydroborate to an aqueous solution of copper(II) sulfate.

When poly(ethylene oxide) and β-cyclodextrin were used as protective polymers, copper particles rapidly coaggregated, and black precipitates were formed in a few minutes under virtually colorless supernatant. No reduction of copper(II) sulfate occured in the presence of poly(acrylic acid), poly(2-acrylamido-2-methyl-1-propanesulfonic acid), or the copolymer of methyl vinyl ether and maleic acid, even after the addition of sodium tetrahydroborate. Poly(aminoethylene) and soluble nylon did not dissolve in aqueous solutions containing copper(II) sulfate due to gelation.

In addition to copper(II) sulfate, copper(II) chloride, copper(II) acetate, and copper(II) nitrate were reduced with sodium tetrahydroborate in the presence of PVP, yielding homogeneous reddish dark brown, dark brown, and dark brown colloidal dispersions, respectively. The dispersion prepared from copper(II) nitrate was rather unstable, and gradually turned into yellowish green even under nitrogen.

Figure 1 shows the absorption spectrum of the colloidal copper dispersion prepared from copper(II) sulfate and PVP (DP=3240). A peak is clearly observed at

Table 2. Effects of Reducing Agents on the Formation of Colloidal Copper Dispersions Using PVP (DP=3240) as Protective Polymer[a)]

Reducing agent	Charged concentration of reducing agent (10^{-2} mol dm^{-3})	Colloid	
		Formation	Color
Sodium tetrahydroborate	*1.0*	*Yes*	*Reddish dark brown*
Hydrazine	3.3	Yes	Reddish brown
Molecular hydrogen	—[b)]	No (no reduction)	—
Ethanol	—[c)]	No (no reduction)	—
Methanol/NaOH	—[d)]	No (precipitation)	—
Formaldehyde	3.3	No (gelation)	—

a) $[CuSO_4]_0=5.0\times10^{-3}$ mol dm^{-3} and [monomeric residue of PVP]$_0=2.0\times10^{-1}$ mol dm^{-3}; solvent was water unless otherwise noted. b) Reduction was carried out at 80 °C, hydrogen pressure 37 atm for 20 h. c) Copper(II) sulfate (0.15 mmol) was refluxed in 50 cm^3 ethanol for 2 h. d) Copper(II) chloride (0.15 mmol) was refluxed in 50 cm^3 of 1:1 methanol-water mixture containing sodium hydroxide (0.45 mmol) for 1 h.

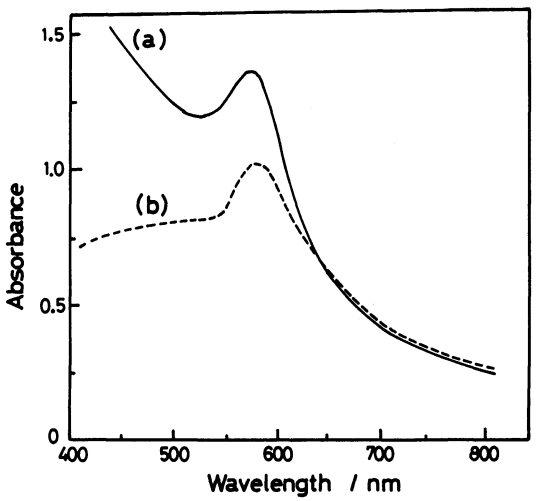

Fig. 1. Absorption spectra for the colloidal copper dispersions prepared by reduction of copper(II) sulfate in the presence of PVP (DP=3240) using (a) sodium tetrahydroborate and (b) hydrazine: $[CuSO_4]_0=5.0\times10^{-3}$, [monomeric residue of PVP]$_0=2.0\times10^{-1}$, $[NaBH_4]_0=1.0\times10^{-2}$, and [hydrazine]$_0=3.3\times10^{-2}$ mol dm^{-3}.

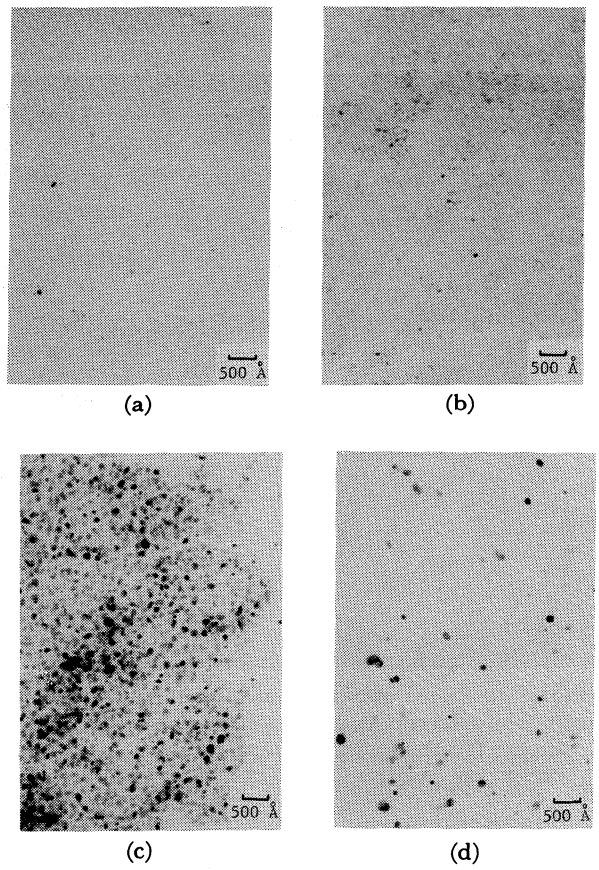

Fig. 2. Electron micrographs of colloidal copper dispersions prepared by reduction of copper(II) sulfate with sodium tetrahydroborate in the presence of (a) PVP (DP=1440), (b) PVP (DP=90), (c) dextrin, or (d) methylcellulose (×100000); $[CuSO_4]_0=5.0\times10^{-3}$, $[NaBH_4]_0=1.0\times10^{-2}$, and [monomeric residue of polymer]$_0=2.0\times10^{-1}$ mol dm^{-3}.

570 nm. Otherwise, the optical density increases with decrease in wavelength, which is ascribed to light scattering by the colloidal copper particles.

Preparation of Colloidal Copper Dispersions Using Various Reducing Agents. Table 2 shows the results of the treatment of copper(II) sulfate with various reducing agents in the presence of PVP (DP=3240). Homogeneous dispersion of copper is prepared with the use of hydrazine as well as sodium tetrahydroborate. The color of the dispersion obtained with hydrazine is reddish brown. As shown in Fig. 1, the dispersion exhibits an absorption miximum at 580 nm.

Colloidal dispersion can not be prepared with the use of the other four reducing agents. Ethanol exhibits no reducing activity on copper(II) sulfate under refluxing conditions. Hydrogen shows no reducing activity at 80 °C under 37 atm either.

Refluxing of alkaline methanol-water mixture (1:1 in volume) containing copper(II) chloride for 10 min turns the color of the solution into pale reddish brown, indicating that a small amount of copper(II) ion is reduced. On prolonged reaction, however, brown precipitates are formed. The addition of formaldehyde to an aqueous solution of copper(II) sulfate and PVP results in gelation.

Electron Microscopy on Colloidal Copper Particles. Figure 2 shows the electron micrographs of the copper

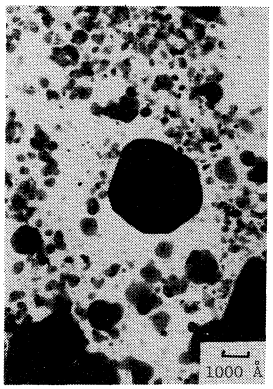

Fig. 3. Electron micrograph of copper precipitates prepared by reduction of copper(II) sulfate in the absence of polymers (×50000); $[CuSO_4]_0=5.0\times10^{-3}$ and $[NaBH_4]_0=1.0\times10^{-2}$ mol dm^{-3}.

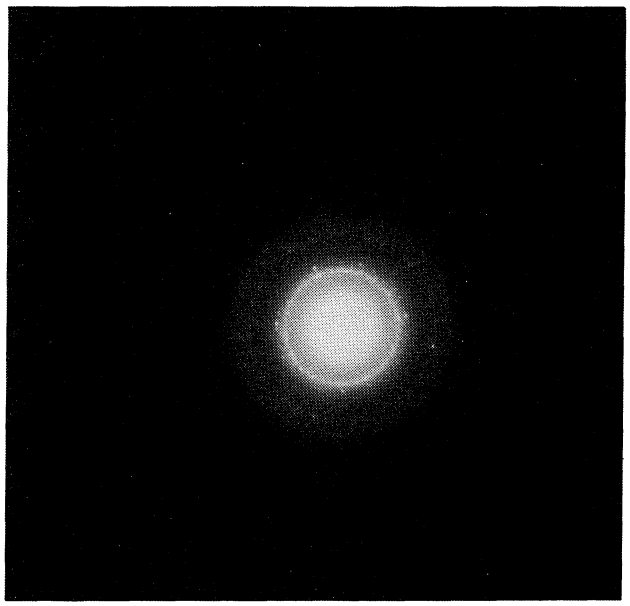

Fig. 4. Selected area electron diffraction pattern of the colloidal copper dispersion obtained by reducing copper(II) sulfate with sodium tetrahydroborate in the presence of dextrin; $[CuSO_4]_0=5.0\times10^{-3}$, $[NaBH_4]_0=1.0\times10^{-2}$, and [monomeric residue of dextrin]$_0=2.0\times10^{-1}$ mol dm^{-3}.

colloids prepared by reduction of copper(II) sulfate with sodium tetrahydroborate in the presence of various polymers. Highly dispersed particles without any aggregation are observed. For the colloid with PVP (DP=1440), for example, the particle size is distributed from 20 to 190 Å, and the average particle diameter is 100 Å. The average diameter depends on the polymer used, ranging from 50 Å for the colloid with PVP (DP=90) to 150 Å for the one with poly(vinyl alcohol) (DP=1500), as listed in Table 1.

In contrast, the diameters of the copper particles in the precipitates, obtained by the reduction of copper(II) sulfate with sodium tetrahydroborate in the absence of the polymers, were widely distributed from 40 to 3500 Å (Fig. 3).

Table 3. Selected Area Electron Diffraction on the Colloidal Copper Dispersion Prepared by Reducing Copper(II) Sulfate with Sodium Tetrahydroborate in the Presence of Dextrin[a)]

Relative radius (r) of Debye-Scherrer ring	Relative ratio for $1/r$	Copper crystal[b)]	
		Lattice[c)] spacing (A)	Relative lattice spacing
1.00	1.93	2.09(111)	1.92
1.17	1.66	1.81(200)	1.66
1.63	1.18	1.28(220)	1.17
1.93	1.00	1.09(311)	1.00

a) $[CuSO_4]_0=5.0\times10^{-3}$ mol dm^{-3}, $[NaBH_4]_0=1.0\times10^{-2}$ mol dm^{-3}, and [monomeric residue of dextrin]$_0=2.0\times10^{-1}$ mol dm^{-3}. b) Values from Ref. 14. c) Numbers in parentheses refer to *hkl* values.

Fig. 5. Electron micrograph of colloidal copper dispersion prepared by reduction of copper(II) sulfate with hydrazine in the presence of PVP (DP=3240) (×100000); $[CuSO_4]_0=5.0\times10^{-3}$, [hydrazine]$_0=3.3\times10^{-2}$, and [monomeric residue of PVP]$_0=2.0\times10^{-1}$ mol dm^{-3}.

Figure 4 depicts a selected area electron diffraction pattern for the particles in the colloidal copper dispersion prepared by reducing copper(II) sulfate in the presence of dextrin. The diffraction experiment has been carried out for the inside of a circle, which is located exactly at the center of the picture (c) in Fig. 2 and has diameter of around 400 nm. Clearly split and distinct Debye-Scherrer rings are observed. Virtually identical patterns are observed also for the dispersions with PVP and poly(vinyl alcohol). As shown in Table 3, the relative ratios for the reciprocals of the radii of the four rings are almost perfectly identical with the relative values for the lattice spacing in pure crystal of bulk copper metal.

Figure 5 shows the electron micrograph of the colloidal copper dispersion prepared by using hydrazine as reducing agent. Copper particles are much larger than those in the dispersions prepared by using sodium tetrahydroborate, and the particle diameters range from 200 Å to 1600 Å.

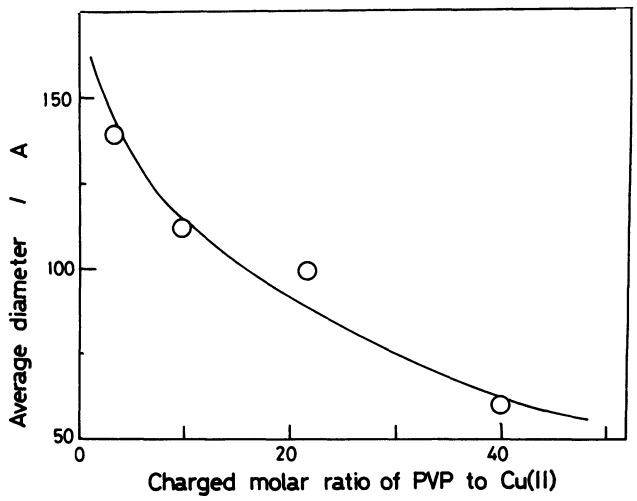

Fig. 6. Dependence of the average diameter of copper particles on the amount of PVP (DP=1440) for the colloidal dispersion prepared by reduction of copper(II) sulfate with sodium tetrahydroborate; $[CuSO_4]_0=5.0\times10^{-3}$ and $[NaBH_4]_0=1.0\times10^{-2}$ mol dm^{-3}.

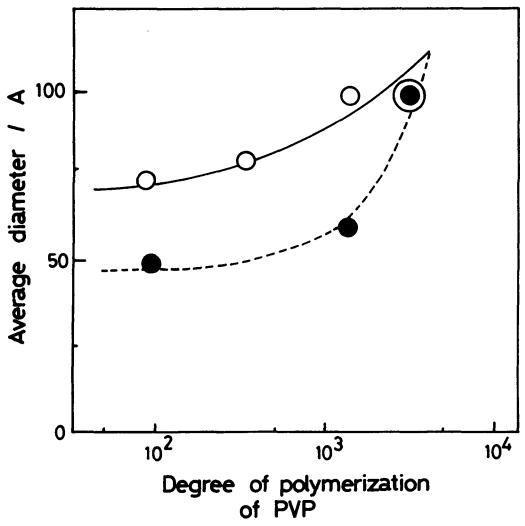

Fig. 7. Dependence of the average diameter of colloidal copper particles on the degree of polymerization of PVP for the colloidal dispersion prepared by reduction of copper(II) sulfate with sodium tetrahydroborate; [monomeric residue of PVP]$_0=1.0\times10^{-1}$ (○) or 2.0×10^{-1} mol dm^{-3} (●); $[CuSO_4]_0=5.0\times10^{-3}$ and $[NaBH_4]_0=1.0\times10^{-2}$ mol dm^{-3}.

Effects of Amount of Poly(*N*-vinyl-2-pyrrolidone) and Its Degree of Polymerization on Size of Copper Particles. As depicted in Fig. 6, the average diameter of copper particles, determined by electron microscopy, monotonously decreases with increase in the charged molar ratio of monomeric residue of PVP to copper(II) sulfate.

Figure 7 shows the plots of the average diameter of copper particles vs. the degree of polymerization of PVP. The particle size increases with increasing degree of polymerization for both the charged molar ratios 20 (○) and 40 (●) of the monomeric residue of PVP to copper(II) sulfate.

Discussion

Formation of Colloidal Copper Particles. Clearly split Debye-Scherrer rings in electron diffraction pattern in Fig. 4, which are virtually identical with those for a crystal of bulk copper metal, show that the colloidal copper particles prepared in the present study are not simple aggregates of copper atoms. Instead, the copper atoms in the particles with diameters of 20—250 Å show face-centered cubic packing in the same way as those in the copper metal. In addition, the lattice constants for the colloidal particles are almost identical with those for bulk copper metal.

Formation of copper boride is ruled out by these facts as well as by successful preparation of colloidal dispersion using hydrazine as reducing agent (Table 2).

The positions of absorption maxima (570 and 580 nm, respectively) for the colloidal copper dispersions prepared by reducing copper(II) sulfate with sodium tetrahydroborate and hydrazine in the presence of PVP (Fig. 1) is almost identical with that (580 nm) for the copper dispersion prepared by using gelatin as protective polymer.[10] The dispersion with gelatin was prepared by reduction of copper(II) sulfate with hydrazine in the presence of gelatin, followed by the removal of large copper particles by centrifugation. These absorption maxima are attributable to excitation of surface plasmon in copper particles.

Protective Polymers. The polymers successfully used as protective polymers for the preparation of colloidal copper dispersions have *N*-substituted amide, alcoholic, ethereal, or sulfate groups in the side chains (Table 1). On the formation of colloidal dispersions, the polymers first form complexes with copper(II) ions using these functional groups. Then copper(II) ions in the polymer complexes are reduced to zero valence states by sodium tetrahydroborate or hydrazine. Stability of the dispersion is attributable to the inhibition of the direct contacts of the metal particles by the polymers, which are located on the surface of the particles.[15]

Steric factors are also important for the polymers to function effectively as protective polymers. Quite a small protecting activity of poly(ethylene oxide) with alkoxyl groups in the polymer main chains, which is in contrast with sufficient protecting activity of poly(methyl vinyl ether) with alkoxyl groups in the side chains, is due to steric hindrance. β-Cyclodextrin, possessing rings composed of seven or fourteen hydroxyl groups with diameter of 6—8 Å, has a poor activity also due to steric hindrance, although poly(vinyl alcohol) shows effective protection. Soluble nylon, which has *N*-unsubstituted amide groups in the main chains and probably interacts with copper(II) ions more strongly than PVP with *N*-substituted amide groups, forms gel

with copper(II) ions.

No reduction of copper(II) ions in the presence of poly(acrylic acid), poly(2-acrylamido-2-methyl-1-propanesulfonic acid), and the copolymer of methyl vinyl ether and maleic acid is associated with the acidity of the polymer complex solution. Here, sodium tetrahydroborate added is largely used for the reactions with protons. This interpretation is consistent with the successful preparation of a colloidal dispersion using poly(potassium vinyl sulfate).

Reducing Agents. Sodium tetrahydroborate and hydrazine effectively reduce copper(II) ions, yielding colloidal copper dispersions. No reducing activity of ethanol and molecular hydrogen on copper(II) ions is in contrast with successful preparation of colloidal dispersions of noble metals from the salts using them as reducing agents.[1,2,6-9] This is attributable to much more negative oxidation-reduction potential (+0.34 eV[16]) for copper(II) ions than those for noble metals. The values for palladium(II), silver(I), and gold(III) ions, for example, are +0.92, +0.83, and +1.50 eV, respectively.[16]

Size of Colloidal Copper Particles. The size of colloidal copper particles should increase with increase in the relative rate of combination of copper atoms with copper particles, with respect to the rate of coverage of surface of copper particles by protective polymers. Thus, the particle size decreases with increasing amount of the protective polymer (Fig. 6). The decrease of the particle size with decreasing degree of polymerization of the protective polymer (Fig. 7) is associated with more rapid and effective coverage of the particles by the polymer of smaller degree of polymerization. This argument is consistent with the fact that the protecting activity of PVP on colloidal dispersions of silver increases with decreasing degree of polymerization.[17]

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