by extrapolation, 0.560%. Therefore, the propagation loss was 14.6 dB/cm.

In conclusion, S-1 and M-1, the vinyl polymer having a pNA unit, possessed a relative low molecular weight and provided glassy polymers transparent in the wavelength region longer than 480 nm. The poled S-1 and M-1 homopolymers possessed high *d* coefficients and good temporal stability at room temperature because of high chromophore concentration and a short spacer group between the polymer main chain and the chromophore unit, and also completely 100% chromophore functionalization. The copolymer of S-1 with M-1 showed drastically low T_g and large temporal decay. On the other hand, the cross-linked copolymer of S-1 with bifunctional S-9 chromophore exhibited more excellent stability than those homopolymers. These materials are expected to be applicable to frequency doubling and EO waveguide devices.

Registry No. S-1, 130525-37-0; S-1 (homopolymer), 130525-38-1; S-2, 139565-77-8; S-2 (homopolymer), 139565-94-9; S-3, 139565-78-9; S-3 (homopolymer), 139565-95-0; S-4, 125038-81-5; S-4 (homopolymer), 139565-96-1; S-5, 139565-79-0; S-5 (homopolymer), 139565-97-2; S-6, 139565-80-3; S-6 (homopolymer), 139565-98-3; S-7, 139565-81-4; S-7 (homopolymer), 139565-99-4; S-8, 139565-82-5; S-8 (homopolymer), 139566-00-0; S-9, 139565-83-6; S-9 (homopolymer), 139566-01-1; M-1, 133547-17-8; M-1 (homopolymer), 139566-02-2; B-1, 43033-22-3; B-1 (homopolymer), 139582-76-6; B-2, 13351-86-5; B-2 (homopolymer), 26375-86-0; (S-1)(M-1) (copolymer), 139566-03-3; (S-1)(S-9) (copolymer), 139566-04-4; $H_2C{=}CHC_6H_4$-*p*-CH_2Cl, 1592-20-7; $H_2C{=}C(CH_3)COCl$, 920-46-7; $HO(CH_2)_2N(CH_3)C_6H_4$-*p*-NO_2, 18226-16-9; $H_2C{=}CHOCOCH_3$, 108-05-4.

New Organosols of CuS, CdS, ZnS, HgS, NiS, and Mixed Metal Sulfides in *N*,*N*-Dimethylformamide and Dimethyl Sulfoxide. Preparation, Characterization, and Physical Properties

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Organosols of transition metal sulfides such as CuS, CdS, ZnS, HgS, and NiS in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are prepared by reactions of H_2S with the solutions of $Cu(OAc)_2$, $CdCl_2$, CdI_2, $Cd(OAc)_2$, $Zn(OAc)_2$, $HgCl_2$, and $Ni(OAc)_2$ (OAc = $OCOCH_3$), respectively. Organosols of mixed metal sulfides $Zn_xCd_{1-x}S$ are obtained by reactions of H_2S with DMF solutions of mixtures of $Cd(OAc)_2$ and $Zn(OAc)_2$ in various ratios. Rayleigh scattering studies of these organosols using an Ar laser beam (λ = 488 nm) show that the particle size of the colloidal metal sulfides and the stability of the organosols vary depending on the metal used and on the conditions of the organosol preparation. The organosol of CuS in DMSO shows a particle size of 13-nm diameter which does not change at 25 °C for 3 days. The organosol of CdS (0.1 M) in DMF has a particle size of 8–10-nm diameter. The particle size does not change for 2 weeks at −15 °C under argon atmosphere. Ar laser irradiation at 17 °C causes gradual increase in the particle size up to 30 nm in diameter and subsequent deposition of CdS. Addition of dodecanethiol or tetrabutylammonium bromide to the CdS organosol causes a blue-shift of the peak of the absorption spectrum. Organosols of ZnS, prepared by reaction of H_2S with a DMF solution of $Zn(OAc)_2$, are much less stable than those of CdS and begin to give a precipitate of ZnS after 1 h at room temperature. The light-scattering study reveals that the average particle size of ZnS increases from 17 to 500 nm in diameter during 70 min at room temperature. Addition of acetone, Et_2O, or methanol to these organosols causes precipitation of the corresponding metal sulfides, whose X-ray diffraction patterns agree with the authentic data. Black or orange organosols of HgS are obtained by reaction of H_2S with a DMF or DMSO solution of $HgCl_2$. Recovered solid from the orange organosol by addition of Et_2O shows a diffraction pattern identical with that of α-HgS, while the black organosol shows diffraction pattern due to β-HgS or those assignable to mixtures of α- and β-HgS depending on the preparation conditions. Organosols of NiS, obtained by reaction of H_2S with $Ni(OAc)_2$ in DMSO, do not show observable light scattering due to the relatively small particle size (<4-nm diameter). Electrophoresis of these organosols indicates the presence of negative charge on the metal sulfide particle surface that is similar to the colloidal particles of the metal sulfides in water.

Introduction

The chemistry and physics of the semiconducting metal sulfides have attracted increasing attention in view of the recent rapid development in the practical uses of semiconductor compounds.[1-4] Fine particles of the semiconducting metal sulfides are of particular interest in that their physical properties are not similar to those of the bulk metal sulfides due to the quantum size effect. Fine CdS colloidal particles (ca. 2–4 nm in the diameter) dispersed in water or organic solvents and stabilized by addition of

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Table I. Preparation Conditions and Properties of the Organosols

preparation[a]		properties of organosols			metal sulfide recovered from the organosol[b]
metal salt	solvent	color	stability[c]	av diam,[d] mm	
$Cu(OAc)_2$	DMF	greenish black	3 days at rt	130	CuS
$Cu(OAc)_2$	DMSO	greenish black	3 days at rt	130	CuS
CdI_2	DMF	yellow	14 days at −15 °C	8.4	β-CdS
$Cd(OAc)_2$	DMF	yellow	14 days at −15 °C	[e]	β-CdS
$Zn(OAc)_2$	DMF	colorless	[f]	17	β-ZnS
$Zn(OAc)_2 + Cd(OAc)_2$ (50:50)	DMF	pale yellow	[f]	13 and 58[g]	$Zn_{0.5}Cd_{0.5}S$[h]
$Zn(OAc)_2 + Cd(OAc)_2$ (12:88)	DMF	pale yellow	[f]	22	$Zn_{0.12}Cd_{0.88}S$[h]
$HgCl_2$	DMF	orange	[f]	[e]	β-HgS
$HgCl_2$	DMF	black	[f]	[e]	α- and β-ZnS
$HgCl_2$	DMSO	black	[f]	[e]	α-HgS
$Ni(OAc)_2 \cdot 4H_2O$	DMSO	black	3 days at rt	[i]	NiS[i]
$Mn(OAc)_2 \cdot 4H_2O$	DMF	black	[f]	[e]	γ-MnS
$Pd(OAc)_2$	DMF	orange	[f]	[e]	PdS[h]

[a] See Experimental Section for the detailed procedure. [b] The metal sulfide was obtained by addition of acetone to the organosols, and characterized by means of elemental analyses as well as X-ray diffraction. [c] Under the shown conditions the organosol did not show any significant change in the particle size under argon atmosphere. See text for the detail. rt = room temperature. [d] Measured by light scattering method. [e] Not measured. [f] The organosol is not stable and causes gradual precipitation of the metal sulfides on standing at room temperatures. [g] Two peaks are observed in particle size distribution. [h] Phase of the solid product was not determined due to broad peak width or absence of peaks in the diffraction pattern. [i] Averaged diameter of NiS in the organosol was not determined probably due to the small particle size.

thiols, organic polymers, and surfactants have been reported to show a blue-shift of the threshold of absorption[5b,c,e,6c,7a,8–10] and also of the fluorescence band[5c–e,6,7,10–13] with decrease of the particle size. Unique reactivity of fine CdS particles has also been reported.[14] Another interest in the colloidal metal sulfides is their use as a source of composite material of the semiconducting compounds in polymer matrices. Composites of inorganic electrically conducting materials such as graphite carbon[15] and copper sulfide[16] with polymers have already been reported. Preparation of homogeneous polymer composites with both good electric properties and plasticity requires inorganic compounds with fine particle size and sharp particle size distribution. Organosols of the metal sulfides that can dissolve various organic polymers are promising as materials for these composites. Very recently preparation of organic polymers or zeolites including small particles of metal sulfides were performed using metal sulfide colloidal solutions which included large amount of organic additives to stabilize the fine particles.[6b,17–19]

Recently we reported in a preliminary communication a general procedure of formation of the metal sulfides as fine particles in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) by adding H_2S to the solutions of the transition metal compounds:[20]

$$MX_2 + H_2S \xrightarrow{\text{DMF or DMSO}} MS\ (\text{organosol}) \qquad (1)$$

$$M = Cd, Cu, Hg, Ni, Zn;\ X = Cl, I, OCOCH_3$$

One of the characteristics of the above organosols is that additives such as polymers and surfactants are not required to stabilize the colloidal particles. The organosols thus obtained are suitable for the preparation of homogeneous electrically conducting composite films by simply mixing them with polymers followed by removing the solvent.

We report here the full details of the preparation and characterization of the organosols of the metal sulfides in order to compare the stability among these organosols, depending on the type of metals and the preparation conditions. Analytical and X-ray diffraction characterization of the metal sulfides recovered from these organosols are also described. The formation of composites of the metal sulfides with polymers from the organosols and their practical applications have been indicated in our preliminary communications.[21]

Experimental Section

The preparation and storage of the organosols were performed under argon or nitrogen atmosphere. H_2S was generated by an

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aqueous reaction of 85% H_3PO_4 with Na_2S, dried by passing P_2O_5, and stored in a glass bulb connected with a vacuum line. The measurement of the volume of H_2S was performed by means of a mercury manometer.[22] DMF and DMSO were dried in the usual manner, distilled, and stored under nitrogen or argon. Tetrabutylammonium bromide (TBAB) was used as purchased from Tokyo Kasei Co.

The elemental analyses were carried out using a Yanagimoto MT-2 CHN autocorder and a Yazawa halogen and sulfur analyzer. The cadmium was analyzed at Showa Denko Co. Ltd. after the sample was burnt by applying high-frequency electromagnetic energy. The UV–vis spectra were measured on a Hitachi 200-20 spectrophotometer. X-ray diffraction patterns were obtained on a Phillips PW-1051 diffractometer using Cu Kα radiation. The magnetic susceptibility was measured on a Shimadzu MB100 magnetic balance in a magnetic field of 7400 G at 23 °C. The Rayleigh scattering study was carried out based on the already reported procedure.[23] Electrophoresis was carried out in a U-shaped glass vessel equipped with a nitrogen inlet and two platinum plate electrodes (1 cm × 2 cm) with a 100-V electric source.

Table I summarizes preparation conditions and physical properties of the obtained organosols as well as diffraction data of the metal sulfides recovered from the organosols.

Preparation of CuS Organosol. A DMF (50 mL) solution of $Cu(OAc)_2$ (0.91 g, 5.0 mmol) was evacuated by repeated freeze and thaw processes. H_2S (370 mL, ca. 15 mmol) was introduced by a vacuum-transfer procedure. The green solution became dark brown and then greenish black with the precipitation of a black solid. The solid was filtered under a stream of nitrogen, washed with acetone, and dried in vacuo (product A, 120 mg). The filtrate was analyzed by Rayleigh scattering as an organosol of CuS with a particle size of 130-nm diameter. The filtrate did not give any precipitate for a week at −20 °C. The addition of acetone to the filtrate caused the precipitation of a black solid, which was filtered, washed with acetone, and dried in vacuo (product B, 320 mg). Anal. Calcd for CuS: S, 33.5. Found: S, 33.5. X-ray diffraction patterns of products A and B show peaks at $2\theta = 27.1°, 27.7°, 29.2°, 31.3°, 32.3°, 47.7°, 52.1°$, and $59.1°$ (the corresponding d = 3.29, 3.22, 3.06, 2.86, 2.77, 1.91, 1.76, and 1.57 Å, respectively) whose positions and relative intensities agree with those of authentic data of CuS.

The organosol of CuS in DMSO was prepared similarly.

Preparation of CdS Organosol. A DMF (150 mL) solution of CdI_2 (5.5 g, 15 mmol) was evacuated by repeated freeze and thaw processes. H_2S (1100 mL, ca. 46 mmol) was introduced by vacuum transfer and the reaction mixture was stirred at 20–25 °C. The colorless solution turned golden yellow immediately. The solution was kept under argon. Similar organosols of CdS were obtained by reaction of $CdCl_2$ and $Cd(OAc)_2$ with H_2S.

The addition of acetone (100 mL) caused the formation of a yellow solid, which was filtered, washed with acetone several times, and dried in vacuo. Anal. Calcd for CdS: Cd, 77.8; S, 22.2; I, 0.0; C, 0.0; H, 0.0; N, 0.0. Found: Cd, 73.2; S, 20.6; I, 0.8; C, 0.2; H, 0.1; N, 0.0. The powder X-ray diffraction pattern of the solid product showed somewhat broadened peaks (half-width = 1.1–1.3° in 2θ) at $2\theta = 26°, 44°$, and $52°$ (the corresponding d = 3.4, 2.1, and 1.8 Å, respectively) which were assigned to the (111), (220), and (311) diffraction line of β-CdS, respectively. The peak intensity ratio corresponded with that of the authentic sample. No peak at $2\theta = 48°$ (d = 1.9 Å), the position of the (103) diffraction line of α-CdS, was observed in the diffraction pattern.

Addition of Dodecanethiol to the CdS Organosol. A CdS organosol in a concentration of 4 mM Cd was prepared from the reaction of CdI_2 (74 mg, 0.2 mmol) with H_2S (0.6 mmol) in DMF (50 mL), in a manner similar to the above procedure. The UV–vis spectrum after dilution of the organosol with DMF to 0.08 mM Cd showed an absorption threshold at 510 nm. To the organosol (5 mL, 0.08 mM Cd) was added dodecanethiol (400 mg, 2.0 mmol) at 3 °C. The UV–vis spectrum of the resulting mixture showed an absorption threshold at 500 nm. A similar addition of 2,2-dimethyl-1-decanethiol to the CdS organosol caused a shift of the threshold of the absorption from 510 to 505 nm.

An organosol prepared by the reaction of H_2S (0.6 mmol) with a mixture of CdI_2 (74 mg, 0.2 mmol) and dodecanethiol (200 mmol) in DMF produced a yellow color and showed a threshold of absorption at 470 nm in the UV–vis spectrum. An organosol prepared similarly by the reaction of H_2S with a mixture of CdI_2 and 2,2-dimethyl-1-decanethiol showed a threshold of 485 nm.

Addition of Tetrabutylammonium Bromide to the CdS Organosol. A CdS organosol in the concentration of 4 mM Cd was prepared from the reaction of CdI_2 (74 mg, 0.2 mmol) with H_2S (0.6 mmol) in DMF (50 mL), in a manner similar to the above procedure. To the organosol (5 mL, 4 mM Cd) was added tetrabutylammonium bromide (640 mg, 2.0 mmol) at 3 °C. The color of the solution changed immediately from yellow to colorless. The UV–vis spectrum of the resulting mixture showed a shoulder at 330 nm. The spectral change was observed while the reaction mixture was allowed to stand at room temperature. Heating the resulting organosol at 100 °C caused a color change from colorless to yellow.

Preparation of ZnS Organosol in DMF. H_2S (600 mL, ca. 25 mmol) was introduced to a DMF (50 mL) solution of $Zn(OAc)_2$ (2.0 g, 11 mmol) to give ZnS organosol as a transparent colorless solution. Depending on the preparation conditions the reaction gave a somewhat milky ZnS organosol from which a transparent organosol was obtained by filtration. Keeping the organosol for 7 h at room temperature gave ZnS as a white precipitate whose X-ray diffraction pattern agrees with that reported for β-ZnS. The addition of MeOH to the organosol also caused a precipitation of ZnS which was washed with MeOH and dried in vacuo (0.88 g, 100%). Anal. Calcd for ZnS: S, 32.9%. Found: S, 31.9%.

Attempts to prepare an organosol of ZnS by reaction of H_2S with the DMF solution of $ZnCl_2$ and ZnI_2 also give a similar transparent reaction mixture. However, the recovered solid by the addition of MeOH to the mixture contained considerable amounts (ca. 10%) of the halogen.

Preparation of $Zn_xCd_{1-x}S$ Organosol in DMF. H_2S (600 mL, ca. 25 mmol) was introduced to a DMF (50 mL) solution of a mixture of $Zn(OAc)_2$ (1.2 g, 6.5 mmol) and $Cd(OAc)_2$ (1.5 g, 6.5 mmol) at room temperature. The reaction mixture turned milky, accompanied by the formation of a small amount of suspended particles. The filtration of the mixture under argon atmosphere gave a transparent pale yellow organosol of $Zn_{0.5}Cd_{0.5}S$.

The addition of Et_2O (100 mL) to the organosol caused a precipitation of the mixed metal sulfide, which was filtered, washed with MeOH, and dried in vacuo (1.4 g, 100%).

The organosols of the other $Zn_xCd_{1-x}S$ (x = 0.12, 0.20, 0.25, 0.80, 0.88) were obtained similarly.

Preparation of HgS Organosol in DMF. H_2S (410 mL, ca. 17 mmol) was introduced into a solution of $HgCl_2$ (2.3 g, 8.5 mmol) in DMF (60 mL) at 18 °C. The initial colorless solution turned black and finally to orange. After stirring the mixture for 30 min an orange solid began to precipitate.

The reactions at lower temperature such at −60 and −50 °C gave a black reaction mixture after stirring for several hours. X-ray diffraction patterns of the recovered solid from the organosol by the addition of acetone revealed the presence of both α- and β-HgS. The peak intensity ratios of the diffractions at $2\theta = 26.1°$ and $31.0°$ (d = 3.41 and 2.88 Å, respectively) were 60:40 and 47:53, respectively, in these two samples. Eleven mixtures of authentic α- and β-HgS prepared separately showed the same correlation between the peak intensity ratio and composition of the α- and β- forms. On the basis of comparing the peak intensities of the above two products with those of the authentic samples, the compositions were obtained as 36:64 and 82:18, respectively.

A similar reaction using a much smaller amount of $HgCl_2$ (0.14 g, 0.52 mmol) in DMF (50 mL) gave a black solution even after stirring for several hours at room temperature. The black solid that was recovered by adding acetone to the organosol shows an X-ray diffraction pattern that was identical to that of β-HgS.

Preparation of HgS Organosol in DMSO. H_2S (410 mL, ca. 17 mmol) was introduced into a DMF (50 mL) solution of $HgCl_2$ (1.4 g, 5.2 mmol) to give a black mixture. The organosol, obtained by the filtration of the formed solid, began to precipitate as a black solid in 30 min to 1 h. The addition of acetone to the organosol caused a precipitation of HgS as a black solid. The solid product recovered from the organosol after 2 h reaction shows

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X-ray diffraction peaks due to β-HgS exclusively. The solid recovered from the organosol kept longer at room temperature shows diffraction peaks due to α-HgS as well.

Preparation of NiS Organosol in DMSO. H_2S (500 mL, ca. 22 mmol) was introduced to a DMSO (100 mL) solution of $Ni(OAc)_2 \cdot 4H_2O$ (2.5 g, 10 mmol) to cause a color change from green to black. Keeping the solution for 12 h caused a precipitation of a black precipitate of NiS. The filtration of the mixture under argon atmosphere gave a black organosol.

The addition of acetone to the organosol gave a black solid which showed sulfur analytical results close to those reported for NiS. Anal. Calcd for NiS: S, 35.3. Found: S, 33.3.

Preparation of MnS through an Organosol. To a DMF (60 mL) solution of $Mn(OAc)_2 \cdot 4H_2O$ (1.6 mmol) was added H_2S (13 mmol) at room temperature. The pink color of the solution turned orange immediately. An orange solid began to precipitate gradually from the reaction mixture. After 2 days the precipitation was complete and the solid was collected, washed with acetone several times and dried in vacuo (0.51 g, 89%). Anal. Calcd for MnS: S, 38.1. Found: S, 36.9. The X-ray diffraction pattern shows peaks at 2θ = 25.9, 27.7, 28.7, 37.0, 45.6, and 53.0° (d = 3.44, 3.22, 3.11, 2.43, 1.99, and 1.73 Å, respectively), which corresponded to the (100), (002), (101), (102), (110), and (220) diffraction of γ-MnS, respectively.

Preparation of Palladium Sulfide through an Organosol. To a DMF (50 mL) solution of $Pd(OAc)_2$ (100 mg, 0.46 mmol) was added H_2S (23 mL, ca. 0.93 mmol) at room temperature. The color of the solution changed immediately from brown to black. The UV–vis spectrum in the range 270–800 nm showed a broad absorption over the observed region. Allowing the organosol to stand caused a gradual precipitation of a black solid. The addition of acetone to the organosol caused the precipitation of PdS as a black solid. Anal. Calcd as PdS: S, 23.2. Found: S, 27.9. The X-ray diffraction pattern of the solid showed a quite broadened peak (half-width >4° in 2θ) near 2θ = 30–35° (d = 3.0–2.6 Å) which consisted of the (120) and (210) diffraction lines of PdS. These diffraction features were common to commercially obtained PdS.

Hydrogenation of Diphenyl Acetylene Catalyzed by Palladium Sulfide Obtained from the Organosol. Palladium sulfide obtained as above (70 mg, ca. 0.51 mmol as PdS) and a *tert*-butyl alcohol (10 mL) solution of diphenyl acetylene (570 mg, 3.2 mmol) were introduced into a stainless steel autoclave. After the evacuation of the system, hydrogen (15 atm) was charged at room temperature. After heating the reaction mixture at 120 °C for 20 h, GC and GC-MS analyses of the mixture indicated the formation of diphenylethane (55%) and *trans*-stilbene (32%). A similar hydrogenation at 180 °C in toluene gave diphenylethane and *trans*-stilbene in 51% and 47% yields, respectively.

Results and Discussion

Organosol of CuS. Reaction of H_2S with $Cu(OAc)_2$ (OAc = $OCOCH_3$) in DMF gives an organosol of CuS accompanied by precipitation of black CuS (organosol:solid ca. 3:1):

$$\mathrm{Cu(OCOCH_3)_2} + \xrightarrow{\text{DMF or DMSO}} \underset{\text{organosol}}{\mathrm{CuS}} + \underset{\text{solid}}{\mathrm{CuS}} \qquad (2)$$

After separation of the solid by filtration the obtained organosol does not give any precipitate for three days at room temperature and for a week at −20 °C. An organosol of CuS in DMSO is obtained similarly by reacting H_2S with $Cu(OAc)_2$ in DMSO followed by filtration of the precipitated CuS. Table II summarizes the results of Rayleigh scattering analysis of the CuS organosol. The average diameter of the particles obtained is 130 nm and does not change for 3 days. Distribution of the particle size is relatively sharp judging from the $\mu^2\Gamma^{-2}$ values (<0.10) where Γ and μ stand for the mean line width of the scattered light and the moment, respectively.[24]

The addition of acetone to the organosols in DMF and DMSO causes precipitation of CuS as a black solid which shows a satisfactory sulfur analytical result for CuS. Both CuS deposited in reaction 2 and CuS recovered from the organosol show X-ray diffraction patterns which agree with the authentic data of CuS.[25] These results indicate that the organosols contain CuS exclusively as the copper-containing compound.

Table II. Light Scattering of CuS Organosol in DMF[a]

time, min	10^{-3} × intensity,[b] s^{-1}	$\Gamma \sin^{-2}(\theta/2)$[c]	diam, nm	$\mu^2\Gamma^{-2}$[c]
0	53.8	2378	130	0.10
5	54.1	2364	130	0.08
10	53.6	2350	130	0.05
100	50.0	2397	130	0.09
105	50.3	2347	130	0.07
3 days			130	

[a] Measured at 25 °C. [b] Scattered light was measured with a photocounting system. Pulse per second values observed are shown. [c] θ, angle of the light scattering; Γ, mean line width of the scattered light; μ, moment. See ref 23 for details.

Table III. Light Scattering of the CdS Organosol in DMF[a]

sample	time, h	10^{-3} × intensity,[b] s^{-1}	10^{-4} Γ × $\sin^{-2}(\theta/2)$	diam, nm	$\mu^2\Gamma^{-2}$
A[c]	0	4.18	5.71	11	0.44
	1	1.80	3.75	16	0.32
	22	0.75	2.09	30	0.25
	25	0.66	2.08	30	0.43
B[d]	0	27.8	7.26	8.4	0.16
	1	17.6	6.48	9.4	0.15
	2	14.0	5.71	11	0.16
	7	7.2	4.03	15	0.22

[a] Measured at 17 °C. [b] Scattered light was measured with a photocounting system. Pulse per second values observed are shown. [c] Organosol kept for 14 days at −15 °C after preparation. [d] Organosol kept for 10 h at −15 °C after preparation.

Organosol of CdS. When dry H_2S was introduced into a DMF solution of CdI_2 (0.1 M) at 15 °C, the colorless solution rapidly turned yellow or yellow–orange showing the formation of CdS:

$$\mathrm{CdX_2} + \mathrm{H_2S} \xrightarrow[\mathrm{X\,=\,Cl,\ I,\ OCOCH_3}]{\text{DMF or DMSO}} \mathrm{CdS}\ (\text{organosol}) \qquad (3)$$

The solution, which looked homogeneous, was maintained for more than 3 days at 15 °C and for more than 2 months at −15 °C under argon atmosphere. After these periods a gradual precipitation of an orange solid is observed. The stability of the organosol depends on the cadmium concentration. The organosols containing 0.2 and 1.0 M CdS similarly prepared begin to precipitate orange CdS after keeping them for 3 days and 1 day at −15 °C, respectively, indicating that the organosol is stable in the lower CdS concentration. The organosol of CdS is also obtained by reactions of H_2S with DMF solutions of $CdCl_2$ and $Cd(OAc)_2$ and with a DMSO solution of CdI_2.

The absorption spectra of the organosols containing CdS at 1.3×10^{-4}–4.2×10^{-4} M show a shoulder at 450 nm on

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[24] As for the definitions of μ and Γ, see ref 23.

[25] The authentic diffraction data of the metal sulfides were taken from the ASTM data. (a) CuS: *Powder Diffraction File Sets 6-10 (Revised)*; Smith, J. V., Ed.; American Society for Testing and Materials: Philadelphia, 1967; p 6-0464. (b) α-CdS: *Ibid.* 6-0314. (c) β-CdS: *Ibid.* 10-0454. (d) α-ZnS: *X-Ray Powder Data File. Sets 1-5 (Revised)*; Smith, J. V., Ed.; American Society for Testing and Materials: Philadelphia, 1967; p 5-0492. (e) β-ZnS: *Ibid.* 5-0566. (f) α-HgS: *Powder Diffraction File Sets 6-10 (Revised)*: Smith, J. V. ed.: American Society for Testing and Materials: Philadelphia, 1967; 6-0256. (g) β-HgS: *ibid.* 6-0261. (h) γ-MnS: *X-Ray Powder Data File. Sets 1-5 (Revised)*; Smith, J. V. ed.; American Society for Testing and Materials: Philadelphia, 1967; 3-1062. (i) PdS: *Powder Diffraction File Sets 25-26*: McClune, W. F. ed.; American Society for Testing and Materials: Philadelphia, 1984; 25-1234.

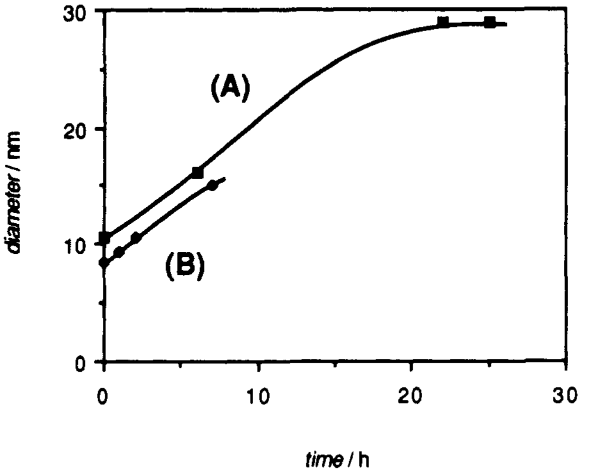

Figure 1. Time course of the particle size of the CdS organosol in DMF. Measurement was performed at 17 °C under irradiation of Ar laser beam ($\lambda - 488$ nm). (A) Organosol kept for 14 days at −15 °C before the measurement; (B) organosol kept for 10 h at −15 °C before the measurement.

the absorption at 270 nm. The peak position is constant among these CdS concentrations. The absorption peak intensity at 450 nm is almost proportional to the CdS concentration, and the obtained absorption coefficient ϵ_{450} (molar absorption coefficient for CdS) is 660. Since the bulk CdS has been reported to have an absorption peak at 480 nm,[26] the peak of the CdS organosol is shifted to a higher energy than that of bulk CdS.

Table III and Figure 1 summarize results of light-scattering studies on the CdS organosol using Ar laser (λ = 488 nm). The CdS in the organosol exists in the form of small particles (8–10-nm diameter) initially. The organosol prepared as described above and stored for 2 weeks at −15 °C (A, Table III, Figure 1) contains CdS particles with an average diameter of 11 nm. Monitoring these solutions by the laser scattering technique at 17 °C indicates an increase in the particle size with time reaching 16 nm in diameter after 7 h and 30 nm after 22 and 27 h. On further standing at 17 °C under irradiation of an Ar laser, the precipitation of CdS starts after about 30 h. Since the organosol is stable for 3 days at 15 °C without irradiation, the growth of the colloidal particle seems to be promoted by the irradiation. CdS organosol similarly prepared and kept for 10 h at −15 °C after preparation (B, Table III, Figure 1) has a particle size of 8.4 nm in the diameter before the irradiation. The Ar laser irradiation of the organosol B causes an increase in the particle size at a rate similar to that of A.

The intensity of the scattered light decreases significantly during the reaction. One of the reasons may be an increase in the absorption intensity of the CdS particle at λ = 488 nm due to an increase in the particle size during the irradiation. The intensity of the scattered light of the CdS organosol A kept for 2 weeks (11-nm diameter) is significantly lower than that of B kept for 10 h (8-nm diameter), indicating that the decrease in the intensity of the scattered light occurs to a considerable extent regardless of the particle size. At present the reason for the decrease of the scattered light intensity is not clear.

The addition of acetone to the DMF organosol causes a precipitation of a yellow solid which contains an almost negligible amount of iodine. Analytical results for S are close to that of CdS. The X-ray diffraction pattern of the obtained solid shows broad peaks (half-width = 1.1–1.3° in 2θ) at 2θ = 26°, 44°, and 52° (d = 3.4, 2.1, and 1.8 Å), respectively, indicating the formation of β-CdS. Depending on the conditions of the organosol preparation and the addition of acetone, a mixture of α- and β-CdS is sometimes deposited. Since the transformation between α- and β-CdS occurs easily even in the solid state,[27] the structure of the CdS can vary in the organosols depending on the conditions. CdS once precipitated is no longer soluble in DMF under any conditions tested, indicating that the cadmium sulfide is soluble only in a metastable state.

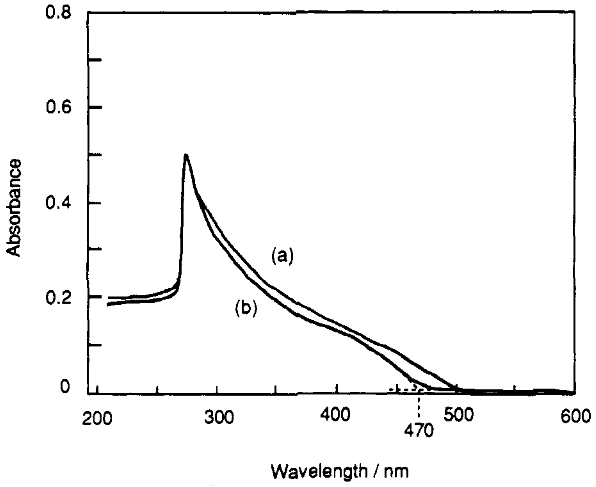

Figure 2. UV–vis spectra of the CdS organosols in DMF (a) prepared from the reaction of H_2S with a DMF solution of CdI_2 and (b) prepared from the reaction of H_2S with a DMF solution of a mixture of CdI_2 and dodecanethiol. The concentrations of CdS, H_2S, and the thiol contained in a and b are 0.08, 0.16, and 80 mM, respectively.

Addition of Thiols to the Organosol. Several colloidal CdS dispersions in water and in organic solvents already reported[5–13] were stabilized by adding polymers, thiols with long alkyl chains, or surfactants. Thiol-stabilized organosols of CdS particularly show a particle size (2–4-nm diameter) which is small enough to show a physical behavior due to the quantum size effect. Although the colloidal CdS in the present study does not require such additives to stabilize it, it has a somewhat larger particle size than the above organosols with thiols. The addition of thiol and surfactants to the organosol of CdS in DMF was performed in order to examine decreased in the particle size.

Figure 2a shows the absorption spectrum of the CdS organosol which shows a threshold of the absorption at 510 nm. The addition of dodecanethiol to the organosol causes a slight shift of the threshold to 500 nm. The organosols are yellow both before and after addition of the thiol. The CdS organosol prepared by the addition of H_2S to a mixture of CdI_2 and dodecanethiol in DMF appears greenish yellow. The UV–vis spectrum (Figure 2b) shows a shift of the shoulder at about 450 nm (see above, Figure 2a) on the absorption at 270 nm to about 410 nm and the threshold of absorption at 470 nm. The blue-shift of the absorption caused by addition of the thiol can be attributed to a small decrease in the particle size of CdS. The variation in the threshold of the absorption among the organosols with the thiol addition observed, depending on the addition procedure in the preparation, indicates that the particles exist in a metastable state.

On the other hand, the addition of tetrabutylammonium bromide (TBAB) to the organosol of CdS causes a drastic color change from yellow to pale yellow initially and then to colorless. Figure 3 shows the change of the absorption

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(26) Hall Jr., J. F. *J. Opt. Soc. Am.* **1956**, *46*, 1013.

(27) Ahlburg, H.; Caines, R. *J. Phys. Chem.* **1962**, *66*, 185.

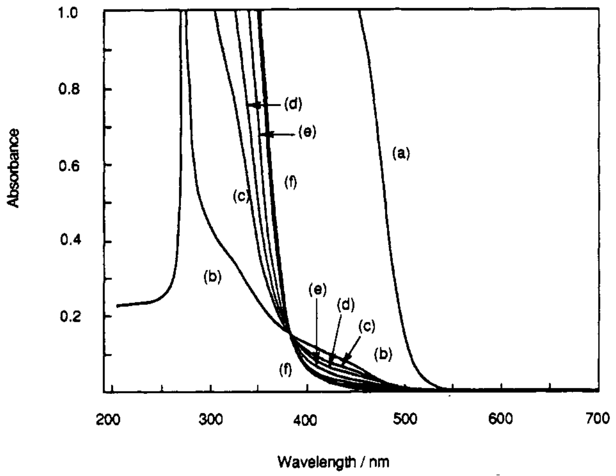

Figure 3. Change of the UV-vis spectra of the CdS organosol with and without added tetrabutylammonium bromide (TBAB) at room temperature. (a) Before addition; (b) 0 h, (c) 1 h, (d) 2 h, (e) 3 h, and (f) 4 h after addition of TBAB (400 mM, TBAB:Cd = 100:1).

spectrum. The spectrum, soon after adding TBAB to the organosol (Figure 3b), shows a shoulder at 330 nm and the threshold of the absorption at 500 nm, indicating a considerable blue-shift of the absorption. When the organosol is allowed to stand at room temperature the absorption spectrum changes (Figure 3b–f) presumably due to the rearrangement or coagulation of the CdS particles. However, at room temperature, the organosol containing TBAB remained colorless. On the other hand, heating the organosol at 100 °C causes a change of the colorless organosol to yellow, suggesting an increase in the particle size to a great extent. All these results indicate that the addition of TBAB promotes a decrease in the particle size. A subsequent aggregation of the CdS particles occurs on heating even in the present of TBAB. These results agree with the conclusion that the colloidal CdS particles in the present organosol exists in a metastable state.

Organosol of ZnS. The reaction of H_2S with a DMF solution of $Zn(OAc)_2$ (0.18 M) gives a colorless solution. However, the solution becomes somewhat milky after 1 h at room temperature and turned white after 6 h. Allowing the mixture to stand for 1 h further causes the precipitation of ZnS as a white solid. ZnS is obtained also by the addition of Et_2O to the above organosol. X-ray diffraction pattern of the obtained ZnS shows broad peaks (half width = 2.3–2.6° in 2θ) at ca. $2\theta = 28°$, 48°, and 57° (d = 3.2, 1.9, and 1.6 Å), respectively. The absence of the diffraction peak near $2\theta = 52°$ (d = 1.8 Å), which corresponds to the position of the (103) diffraction line of α-ZnS, indicates the presence of the β-crystal structure of the obtained ZnS:

$$Zn(OCOCH_3)_2 + H_2S \xrightarrow{\text{DMF}} \text{ZnS (organosol)} \xrightarrow{\text{room temp}} \text{ZnS (precipitate)} \quad (4)$$

The absorption spectrum of the ZnS organosol shows a shoulder at ca. 340 nm. The results of the argon laser scattering of the organosol with time are shown in Figure 4. The average diameter of the particles of the ZnS organosol obtained from $\Gamma \sin^{-2}(\theta/2)$ (θ is the angle of scattering) increases with time. The average of $\Gamma \sin^{-2}(\theta/2)$ decreases with time linearly during the initial 45 min. Extrapolation of the line indicates a $\Gamma \sin^{-2}(\theta/2)$ value of 43 000 at the time of preparing the organosol; this value corresponds to an average ZnS particle size of 17 nm in diameter. These results indicate that the colloidal particles of ZnS grow from 17 nm to ca. 500 nm in diameter within 70 min after preparation at room temperature (25 °C) under irradiation. The formation of ZnS particles in the mixture is visually observed after 1 h irradiation under these conditions.

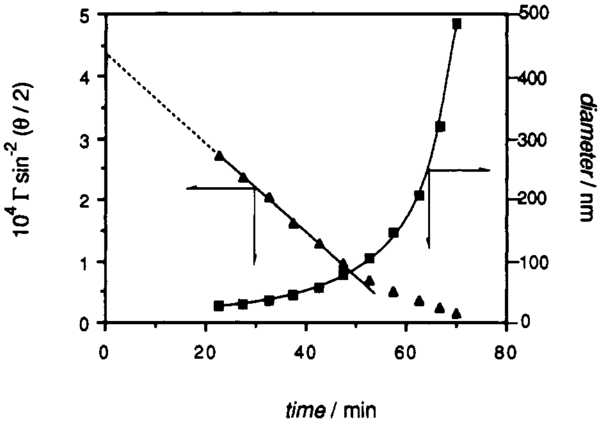

Figure 4. Time dependence of the particle size of the ZnS in DMF. ▲, $\Gamma \sin^{-2}(\theta/2)$; ■, average diameter of the particles obtained from $\Gamma \sin^{-2}(\theta/2)$. Measurement was performed at 17 °C under irradiation of Ar laser beam (λ = 488 nm). The organosol was kept at −15 °C for ca. 3 h and irradiated for 20 min with the Ar laser beam before the measurement.

Organosol of $Zn_xCd_{1-x}S$ in DMF. The reactions of H_2S with DMF solutions of mixtures of $Zn(OAc)_2$ and $Cd(OAc)_2$ give milky white or pale yellow organosols accompanied by the formation of some suspended particles:

$$x\,Zn(OCOCH_3)_2 + [1 - x]Cd(OCOCH_3)_2 + H_2S \rightarrow \underset{\text{organosol}}{Zn_xCd_{1-x}S} \quad (5)$$

$$x = 0.12, 0.20, 0.25, 0.50, 0.80, 0.88$$

The transparent organosols obtained by filtering the solid show a pale yellow color when x is less than 0.80, while an almost colorless organosol is obtained at x = 0.80 and 0.88. These organosols are considered to contain various mixed metal sulfides $Zn_xCd_{1-x}S$ as colloidal particles depending on the ratio of $Zn(OAc)_2$ with $Cd(OAc)_2$ in the starting mixture. The Ar laser scattering analysis reveals that the organosol obtained from a 50:50 mixture of $Zn(OAc)_2$ and $Cd(OAc)_2$ contains particles with size distribution having two peaks centered at 13- and 58-nm diameter, respectively. This seems to suggest the coexistence of the $Zn_xCl_{1-x}S$ particles with different composition in the organosol. On the other hand, the use of an 88:12 mixture of $Zn(OAc)_2$ and $Cd(OAc)_2$ in the reaction with H_2S produces an organosol containing the mixed metal sulfide with a particle size centered at 22-nm diameter. The UV–vis spectrum of the organosol prepared from a 50:50 mixture of $Zn(OAc)_2$ and $Cd(OAc)_2$ shows an absorption peak at 410 nm at room temperature. The peak position is between those of the organosols of ZnS and CdS similarly obtained. CdS–ZnS co-colloids in water have been already prepared from the reaction of $CdCl_2$ and $ZnCl_2$ with H_2S in the presence of Na_3PO_3 under appropriate pH conditions.[5d,28] The threshold of the absorbance of these sols was reported to increase with an increase of the relative ratio of Cd to Zn in the system.

Adding acetone to the present organosols produces mixed Zn–Cd sulfides as a pale yellow to yellow solid that is almost free of carbon and hydrogen. The X-ray diffraction pattern of $Zn_{0.5}Cd_{0.5}S$[29] shows broad peaks (half

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(28) Henglein, A.; Gutiérrez, M. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 852.

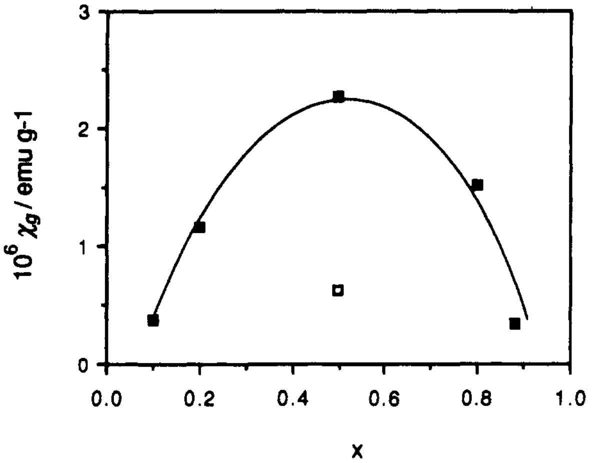

Figure 5. Magnetic susceptibility of $Zn_xCd_{1-x}S$. ■, obtained by addition of Et_2O to the organosols of corresponding mixed metal sulfides; □, after heating $Zn_{0.5}Cd_{0.5}S$ obtained as above for 7 h at 200 °C.

width = 2.3–2.8° in 2*θ*) at 2*θ* = 28°, 46°, and 54° (*d* = 3.2, 2.0 and 1.7 Å), respectively. These peaks are attributed to the (111), (220), and (311) diffraction lines of the cadmium–zinc mixed metal sulfide. The 2*θ* values are smaller than the corresponding peaks of *β*-ZnS and larger than those of *β*-CdS.[30] $Zn_{0.2}Cd_{0.8}S$ shows broad peaks (half width = 1.2–1.5°· in 2*θ*) at 2*θ* = 27°, 44°, 48°, and 53° (*d* = 3.3, 2.1, 1.9, and 1.7 Å), respectively. The presence of the peak at 2*θ* = 48° as well as the clear shoulders at 2*θ* = 27° indicate that it is composed of a mixture of *α*- and *β*- structures. The peak positions are near to those of CdS although the high angle peaks are slightly shifted to those of ZnS. The diffraction of $Zn_{0.12}Cd_{0.88}S$ shows similar features.

An interesting feature of the recovered mixed metal sulfide is that it shows paramagnetism, whereas the nonmixed *β*-ZnS and *β*-CdS recovered from the organosol do not. The magnetic susceptibility of $Cd_xZn_{1-x}S$ is plotted against the *x* value in Figure 5. The 1:1 mixed Zn–Cd sulfide has a magnetic susceptibility of 2.2 × 10^{-6} emu g^{-1} corresponding to the presence of about two unpaired electrons in every $ZnCdS_2$ unit. The magnetic susceptibility of the sulfide is significantly dependant on the *x* values, and $Zn_{0.88}Cd_{0.12}S$ and $Zn_{0.12}Cd_{0.88}S$ show a magnetic susceptibility of about 0.3 × 10^{-6} emu g^{-1}. Heating the sample at 200 °C for 7 h causes a significant decrease in the magnetic susceptibility. The paramagnetism of the mixed-metal sulfide can be partly attributed to the presence of defects such as metal or sulfide vacancy and/or to the presence of dangling bonds generated by local disorder in the crystal structures.

Organosol of HgS. The reaction of H_2S with $HgCl_2$ in DMF or DMSO gives an organosol of HgS similar to that of the other metal compounds. However, the organosol shows an orange or a black color depending on the solvent and the preparation conditions, indicating that the crystalline form of HgS varies with the solvent surrounding the small particle of HgS:

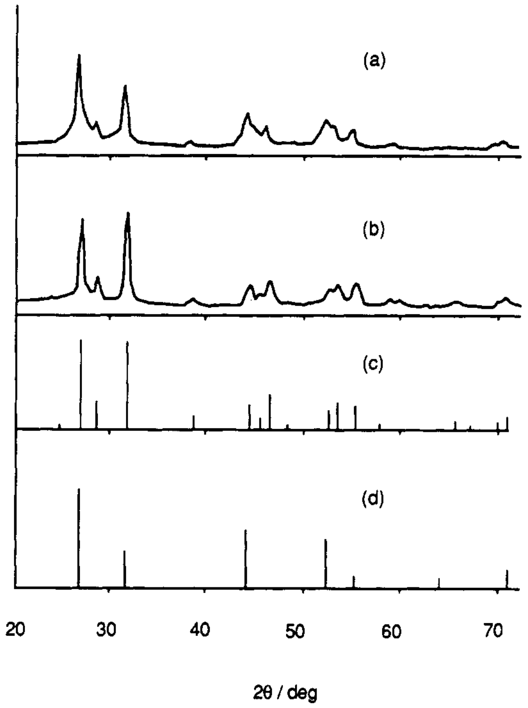

Figure 6. X-ray diffraction patterns of HgS obtained by addition of acetone to (a) organosol prepared and stored at −50 °C in DMF: (b) organosol prepared and stored at −40 °C in DMF. ASTM data of (c) *α*-HgS and (d) *β*-HgS.

$$HgCl_2 + H_2S \xrightarrow{\text{DMF, −60 °C}} \text{HgS (black organosol)}$$
$$\xrightarrow{\text{room temp}} \alpha\text{-HgS (orange organosol)} \quad (6)$$

$$HgCl_2 + H_2S \xrightarrow{\text{DMSO}} \beta\text{-HgS (black organosol)} \quad (7)$$

The reaction of H_2S with $HgCl_2$ in DMF at room temperature and at low concentration (e.g., 0.01 M) of $HgCl_2$ causes a change of the reaction mixture from colorless to black initially and then to orange. The addition of acetone to the organosol causes a precipitation of *α*-HgS which shows an X-ray diffraction pattern identical to that of an authentic sample. At a higher concentration of $HgCl_2$ (0.08–0.14 M), the organosol of *α*-HgS is obtained even at −60 °C. The preparation of the organosol at low temperature and at low concentration of HgS reveals the transition of the HgS structure in the organosol. Figure 6a shows the X-ray diffraction pattern of HgS recovered from the organosols prepared at −50 °C by adding acetone soon after the preparation. Figure 6b shows the diffraction pattern of HgS similarly obtained from the organosol prepared and stored at −40 °C. HgS recovered from the organosol at −50 °C (Figure 6a) shows diffraction peaks at 2*θ* = 26 1° and 31.0° (*d* = 3.41 and 2.88 Å) in the intensity ratio of 60:40, while that from the organosol at −40 °C (Figure 6b) shows these diffraction peaks in the intensity ratio of 47:53. These peaks are assigned to a mixture of the (101) diffraction line of the *α*- form with the (111) diffraction line of the *β*- form and the (200) diffraction line of the *α*- form, respectively. The peak intensity ratios, calibrated by comparison with the diffraction patterns of the authentic samples, indicate that the relative content of the *α*- and *β*- forms in the HgS samples in parts a and b of Figure 6 are 36:64 and 82:18,

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(29) Precise formula of the mixed metal sulfides obtained by addition of Et_2O to the organosols were not determined by means of sulfur and metal analyses. However, high yields of the metal sulfides (>90%) as well as negligible amount of carbon and hydrogen revealed by CHN analyses indicates that the ratio of Zn to Cd in the product is similar to the ratio of $Zn(OAc)_2$ and $Cd(OAc)_2$ used.

(30) Diffraction patterns of $Zn_xCd_{1-x}S$ have been already studied in detail. See: Domens, P.; Cadene, M.; Cohen-Solal, G. W.; Martinuzzi, S.; Brouty, C. *Phys. Status Solidi* **1980**, *59a*, 201 , Rajebhonsale, M. R.; Pawar, S. H. *Indian J. Pure Appl. Phys.* **1982**, *20*, 652. The relative broad peaks in the diffraction pattern of our $Zn_xCd_{1-x}S$ prevented us from detailed investigation of the crystal type. The products in the present study may be composed of physical mixtures of mixed metal sulfides with various ratios of Zn to Cd.

respectively. These results indicate clearly an occurrence of the β → α transition in the organosol near at −50 to −40 °C.

On the other hand, the reaction of H_2S with $HgCl_2$ in DMSO at −60 to 18 °C and at 0.01 to 0.14 M of $HgCl_2$ gives a black organosol. The solid recovered from the organosol obtained from the reaction for 2 h shows only diffraction peaks due to β-HgS, while the solid obtained from the organosol allowed to stand for a longer period shows diffraction peaks attributable to a small amount of α-HgS as well. In summary, the reactions of H_2S with $HgCl_2$ in DMF and in DMSO give β-HgS initially. In DMF the HgS undergoes a rapid transition to the α- form at room temperature and a high concentration of HgS, while the isomerization is much slower in DMSO. Since the transformation of the β- to α- structure of HgS in the solid state is observed at much higher temperature (194 °C),[31] it seems to be facilitated in the organosol particles in which the crystal structure is more flexible than in the bulk HgS. The β → α transition in the organosol is irreversible. When the concentration of HgS is relatively low (ca. 0.01 M), both the orange and the black organosols look transparent for a few hours at room temperature. However, when the concentration of HgS is relatively high (0.08–0.14 M), they are not stable at room temperature; the red organosol causes a precipitation of α-HgS after 20 min and the black organosol causes the precipitation of β-HgS after 2 h.

Organosol of NiS. The reaction of $Ni(OAc)_2$ with H_2S in DMF gives a black solution. The solution is stable under argon atmosphere, but the introduction of air to the reaction vessel causes an immediate precipitation of NiS as a black solid:

$$Ni(OCOCH_3)_2 + H_2S \xrightarrow{\text{DMF, room temp}} NiS \text{ (organosol)} \tag{8}$$

Since the NiS organosol does not show light scattering using the Ar laser (λ = 488 nm), it contains only particles smaller than 2 nm in diameter. The addition of acetone to the organosol causes a precipitation of NiS as a black solid which does not show any X-ray diffraction peaks probably due to the small particle size (<ca. 4 nm in diameter) of the metal sulfide.[32]

Stability of the Organosols. The organosols of the metal sulfides obtained by the above procedures show varying stability depending on the type of the metals. The stability of the organosols is also seriously influenced by the conditions such as the metal sulfide concentration, temperature, and light irradiation. Although the CdS organosol in DMF at 0.1 M concentration is stable for several days at 15 °C, the introduction of air to the organosol causes a gradual precipitation of CdS as an orange solid. Similarly, the organosols of CuS and NiS, which are stable enough under argon atmosphere, begin to precipitate the corresponding metal sulfides on contact with air. The evacuation of the vessel containing CdS organosol, from which H_2S dissolved in DMF is removed, also causes an immediate precipitation of CdS. These results seem to indicate that the particles of metal sulfides in the organosols are quite sensitive toward the atmosphere and that the H_2S dissolved in the organosol helps to stabilize the fine particles to a considerable extent. Recently, the CdS colloidal particles have been prepared using a large amount of thiols as a coexisting stabilizer.[10] The amount of the added thiol is higher than that of the cadmium contained in the sols (ca. 100 equiv) while the organosols contain H_2S in much less amounts (2–3 equiv of Cd). Stabilization of the colloidal particle by the added thiol is attributed to the adsorption of the hydrophilic thiol with its long alkyl chain on the surface of the particles. In some cases the formation of a $Cd(SR)_2$ moiety on the particle surface to give $[CdS]_x[Cd(SR)_2]_{n-x}$ particles has been also suggested.[10]

The metal sulfide recovered from the organosol by the addition of Et_2O, acetone, and MeOH show analytical results or X-ray diffraction data which agree with that reported for the sulfide of the divalent metals. These results argue against the possible formation of $Cd(SH)_2$ moiety in part in the organosols in the present study. The stabilization of fine particles can be attributed to the adsorption of H_2S molecules on the surface of the colloidal particles of the metal sulfides, MS. The H_2S seems to prevent a rapid aggregation of the colloidal particles so as to cause deposition of the metal sulfides as a solid.[6,9,13] Some transition metal sulfides such as ZnS were already known to dissolve in water containing H_2S to some extent although the solubility of the sulfide in water is very low. In this case the H_2S helps to stabilize the fine particles of the metal sulfides similar to the organosol in this study.

Electrophoresis of the present organosols results in deposition of the metal sulfides on the anodic plate accompanied by the generation of H_2, probably derived from H_2S in the system, on the cathodic side. This result indicates that the small particles of the metal sulfides have a negative charge that is similar to the colloidal particles of the metal sulfide in water.

Preparation of Other Metal Sulfides through Organosols and Their Properties. The reactions of H_2S with the other transition metals, palladium and manganese in DMF, followed by the addition of acetone, gives the corresponding sulfides of the metals, respectively. Formation of homogeneous organosols is observed before adding acetone to these reaction mixtures, although detailed studies on the organosol by means of light scattering and electrophoresis were not performed.

Manganese sulfide shows both analytical and diffraction data which agree with those of γ-MnS. Palladium sulfide thus obtained shows a higher analytical value of sulfur than the calculated value for PdS. The X-ray diffraction pattern shows quite a broad peak ($2\theta = 34°$, $d = 2.6$ Å) at the position of the (121) and (211) diffraction lines of PdS. These facts seem to suggest that nonstoichiometric palladium sulfide is formed in part. The palladium sulfide thus obtained catalyzes the hydrogenation of diphenylacetylene to diphenylethane and *trans*-stilbene.

Conclusions

The organosols of CdS, CuS, ZnS, NiS, HgS, and mixed metal sulfides are obtained by the reaction of excess H_2S with the metal salts in DMF and DMSO. The CdS, CuS, and NiS organosols are sufficiently stable for a detailed light-scattering study using Ar laser, if stored under the proper conditions while the other organosols exist only for a relatively short period. These organosols undergo a precipitation of the corresponding metal sulfides upon the addition of acetone, Et_2O, and methanol. Since the organosols do not contain any stabilizing agents such as polymers, thiols, and surfactants, they seem to be suitable as starting materials to prepare composite of the sulfides contained as fine particles in organic polymers and other inorganic matrices.

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and Dr. Masako Tanaka for the elemental analyses of the compounds.

Registry No. TBAB, 1643-19-2; DMF, 68-12-2; DMSO, 67-68-5; CuS, 1317-40-4; CdS, 1306-23-6; ZnS, 1314-98-3; HgS, 1344-48-5; NiS, 16812-54-7; H_2S, 7783-06-4; $Cu(OAc)_2$, 142-71-2; $CdCl_2$, 10108-64-2; CdI_2, 7790-80-9; $Cd(OAc)_2$, 543-90-8; $Zn(OAc)_2$, 557-34-6; $HgCl_2$, 7487-94-7; $Ni(OAc)_2$, 373-02-4; MnS, 18820-29-6; $Mn(OAc)_2$, 638-38-0; PdS, 12125-22-3; $Pd(OAc)_2$, 3375-31-3; diphenylacetylene, 501-65-5; dodecanethiol, 1322-36-7.

Electrically Conductive Metal Sulfide–Polymer Composites Prepared by Using Organosols of Metal Sulfides

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Electrically conducting metal sulfide (MS; M = Cu, Cd, Zn, etc.)–polymer (poly(acrylonitrile), poly(vinyl butyral), poly(vinylidene fluoride), poly[arylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl)], etc.) composite films are obtained by using organosols containing MS and the polymer. The CuS–polymer composite films exhibit electrical conductivities of 1–30 S cm^{-1} at 40 wt % CuS. The CuS–poly[arylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl)] composite film containing 20–40 wt % CuS is thermally stable up to 250 °C, has good mechanical strength (breaking stress of ca. 10^8 Pa), and serves as shielding materials for electromagnetic waves intercepting 99% of the electromagnetic wave at 200 MHz. CdS–polymer composites exhibit electrical conductivities of 10^{-8}–10^{-4} S cm^{-1}, and ZnS–, α-HgS–, NiS–, PdS–, MnS–, and mixed metal sulfide Zn(Cd)S–polymer composites have electrical conductivities in the range 10^{-9}–10^{-4} S cm^{-1}. CuS–polymer and CdS–polymer composites indicate p-type and n-type electrically conductive properties, respectively. The temperature dependence of the electrical conductivity of the MS–polymer composites obeys Arrhenius type equations, giving activation energies of −5.7 kJ mol^{-1} for the CuS–poly(vinyl alcohol) composite (wt % of CuS = 31), 2.8 kJ mol^{-1} for the CuS–80:20 copolymer of vinylidene chloride and acrylonitrile composite (wt % of CuS = 19), and 32 kJ mol^{-1} for the CdS–poly(vinylidene fluoride) composite (wt % of CdS = 43). The electric current is believed to flow through a network of MS formed in the composites. Preparation of MS–polymer composite films on the surface of substrates (e.g., copper sulfide and n-Si) affords heterojunctions, which show rectification of electric current with rate values of 30–102.

Introduction

It is reported in the preceding paper[1,4] that reactions of bivalent transition metal salts with H_2S in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) afford organosols (organic liquid containing colloidal particles) of the corresponding metal sulfides:

$$MX_2 + H_2S \xrightarrow{\text{DMF, DMSO}} \text{MS organosols} \qquad (1)$$

Since DMF and DMSO can dissolve a variety of polymers, the organosol also can dissolve various kinds of polymers in it and can be used as the starting material to prepare various polymer–metal sulfide composites, especially the composites in the form of a film.

Scheme I

$$\text{MS organosol} + \text{polymer} \rightarrow \text{organosol containing MS and polymer} \xrightarrow[\text{(2) evaporation of solvent}]{\text{(1) spreading on plate}} \text{polymer–MS composite (film)}$$

It is known that appropriately prepared polymer composites of some metal sulfides such as CuS[2] and CdS[3] show interesting electrical properties. In cases of the present polymer–MS composites prepared according to Scheme I they also show interesting electrically conductive properties;[4] e.g., some polymer–CuS composites show electrical conductivity (σ) as high as 50 S cm^{-1}, which cannot be attained by mechanical mixing of polymers with CuS powder. In this research various DMF- or DMSO-soluble polymers which form good polymer–metal sulfide composite films have been used. We now report full details of the preparation and electrical properties of the metal sulfide-polymer composites.

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