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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.

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.

Scheme I

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

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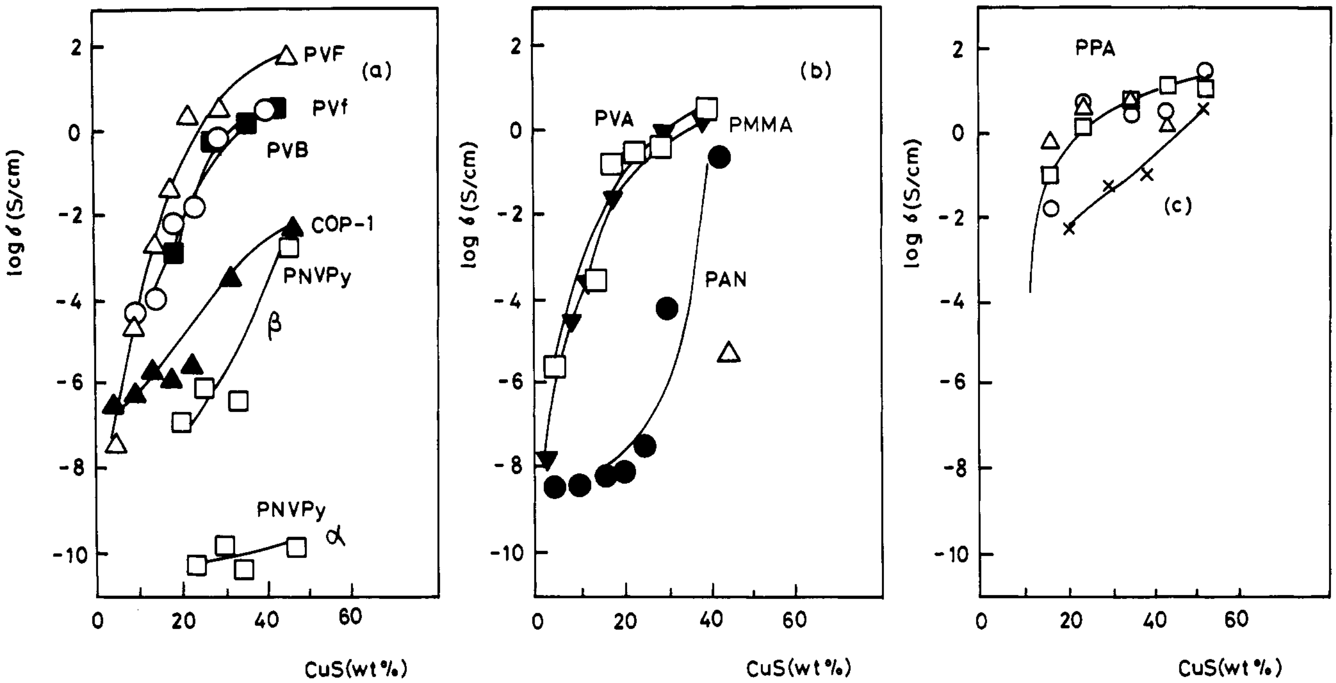

Figure 1. Dependence of the electrical conductivity (σ) of the copper sulfide–polymer composites on the content of copper sulfide prepared according to Scheme I. (a) △ poly(vinyl formal), ■ poly(vinylidene fluoride), ○ poly(vinyl butyral), ▲ copolymer of vinylidene chloride and acrylonitrile (80:20), □ poly(*N*-vinyl-2-pyrrolidone). For poly(*N*-vinyl-2-pyrrolidone), use of DMF gave only a paste showing a low σ value (curve α), and a film was obtained with the DMSO organosol (curve β). (b) □ poly(vinyl alcohol), ▼ poly(methyl methacrylate), ● poly(acrylonitrile). △: Data for CuS–poly(acrylonitrile) composites prepared by using commercially available CuS powder (see the text). (c): ○ poly(parabanic acid) PAA–M–1.0 (see text), □ poly(parabanic acid) PAA–M–0.8, △ poly(parabanic acid) PAA–TM–1.0, × polysulfone $((CH_2)_6SO_2)_n$.

Experimental Section

Materials. Organosols of metal sulfides were prepared as described in the preceding paper.[1,4] Most polymers were purchased from Polysciences Co. Ltd. Poly[arylene(1,3-imidazoline-2,4,5-trione-1,3-diyl)]s were kindly donated by Tonen Sekiyukagaku K.K. Crystalline n-Si (concentration of dopant (P) = 5×10^{15} cm^{-3}; resistivity = 1.0 ± 0.3 Ω cm; with (100)) plate was purchased from Japan Silicon Co. Ltd., and SiO_2 on the plate was removed by treatment with an aqueous solution of HF. The glass plate coated with semitransparent copper sulfide[15] (cf. Table IV) was kindly donated by Nihon Sanmo Dyeing Co. Ltd., and the glass plate showed surface resistance of about 100 Ω/squre. CuS and CdS powders were purchased from Yoneyama Yakuhin Kogyo Co. Ltd. and Koso Chemical Co. Ltd., respectively.

Preparation of Composites. Polymer was dissolved into the organosol of metal sulfide to obtain an organosol containing the metal sulfide and polymer, and the newly obtained organosol looked transparent. The newly prepared organosol was spread on a glass substrate, and solvent was removed under vacuum to obtain the composite film. The prepared film was not transparent in most cases; however, sometimes transparent yellow CdS–poly(acrylonitrile) composite films (wt % of CdS = ca. 50) were obtained. Complete removal of solvent under vacuum was confirmed by IR.

Preparation of the CuS- and CdS–poly(acrylonitrile) composites using the commercially available CuS and CdS powders was carried out as follows: The commercially available CuS powder was ground in an agate mortar, and to the ground CuS powder was added a DMF solution of poly(acrylonitrile). They were mixed in the agate mortar to give a paste, which was spread on a glass plate and dried under dynamic vacuum to give a black film. The CdS–poly(acrylonitrile) composite film was prepared analogously. Mixing of powder CuS and poly(ethylene) in an 80:20 wt/wt ratio in a melting system, which was kindly carried out by Mr. H. Yamada of Lion Corp., gave a plate with dimensions of 2 mm × 13 cm × 13 cm. The plate showed only a low electrical conductivity (1.0×10^{-5} S cm^{-1}).

Measurements. The composite film was cut into rectangular sheet. Both ends of the rectangular film were connected with copper wires by using electrically conducting carbon–polymer paste (Electrodag +502 from Furuuchi Chemicals Co. Ltd.), and the electrical conductivity was measured by a two-probe method with a Takedariken electrometer TR-8651 or from the *I–V* relationship measured with a Hokuto Denko potentiostat/galvanostat HA-301 and function generator HB-104.

IR spectra were recorded on a JEOL-FT/IR-3 spectrometer or a JEOL-IR-810 spectrometer. Thermal analysis of the CuS–poly[arylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl)] composite film was performed under N_2 with Shimadzu DT-30 and TGA-30 thermoanalyzer. Carrier mobilities were measured with a Model-6500 Wafer Mobility Contactless made by Minato Electronics. Mechanical strengths of the composite films were measured at room temperature at Tonen Sekiyukagaku K.K. using rectangular film with 3-mm widths.

Results and Discussion

CuS-Polymer Composites. Figure 1 shows the electrical conductivity (σ) of the CuS-polymer composites prepared according to Scheme I. As shown in Figure 1, the electrical conductivity of the CuS–polymer composites increases with increase in the CuS content reaching 10^{-2}–10^{2} S cm^{-1} at about 40 wt % CuS. Single-crystal CuS is reported[6] to have electrical conductivity of 1.4×10^{4} S cm^{-1}, and the electrical conductivity of the CuS–polymer composites is comparable to or higher than that of carbon–polymer composites.[7] The electrical conductivity is, however, lower than that of metal (e.g., Cu and Ni)–

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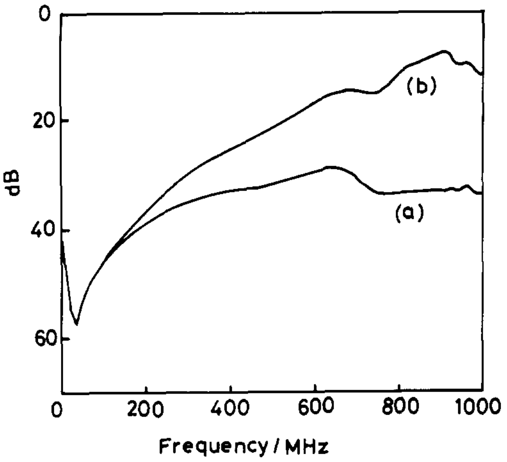
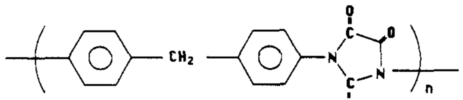


Figure 2. Shielding of electromagnetic waves by the poly(parabanic acid)–CuS composite film. (a) PPA–M–0.8, wt % of CuS = 25 (film thickness = 100 μm, σ = 1 S cm^{-1}); (b): PPA–M–1.0, wt % of CuS = 25 (film thickness = 100 μm, σ = 2 S cm^{-1}).

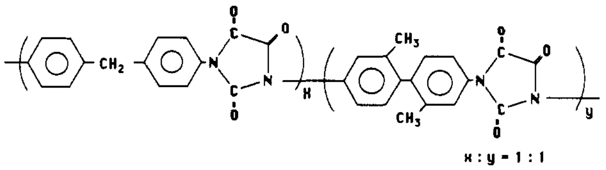
polymer composites. The 40 wt % content of CuS (specific gravity = 4.6 g cm^{-3}) in the composite roughly corresponds to about 13% volume fraction of CuS.

A CuS–poly(acrylonitrile) film prepared by mixing commercially available CuS powder and a DMF solution of poly(acrylonitrile), spreading the mixture on a glass plate, and removal of DMF under vacuum showed considerably lower electrical conductivity than that of the present organosol CuS–poly(acrylonitrile) film as shown in Figure 1b. Mechanical mixing of the commercially available CuS powder with poly(ethylene) (CuS: poly(ethylene) = 80:20 wt/wt) under melting conditions afforded a composite plate which showed the electrical conductivity of 10^{-5} S cm^{-1}.

Among the polymers tested, poly[arylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl)] or poly(parabanic acid) (Figure 1c) having high thermal stability[8] gives a composite with not only the highest electrical conductivity (cf. Figure 1c) but also high mechanical strength and high thermal stability. For example, CuS–PPA–M–1.0 (CuS = 40 wt %), CuS–PPA–M–0.8 (CuS = 20 wt %), and CuS–PPA–TM–1.0 (CuS = 20 wt %) composite films (thickness = 30–50 mm) exhibited breaking stresses of 7.8 × 10^7, 12 × 10^7, and 12 × 10^7 Pa, respectively; the CuS–PPA–TM–1.0 (CuS = 20%) film broke at 37% elongation. The black CuS–PPA composite films showed no observable color change and did not melt up to 250 °C, and their electrical conductivity was essentially unchanged after leaving them for 200 days under air (10–35 °C with ca. 30–100% humidity).



PAA-M-1.0 ([η] = ca. 1.0 dl g^{-1})
PAA-M-0.8 ([η] = ca. 0.8 dl g^{-1})



PAA-TM-1.0 ([η] = ca. 1.0 dl g^{-1})

Owing to their high electrical conductivities, the CuS–PPA films reflect and absorb electromagnetic waves. Figure 2 shows the shielding effect of the films where the coordinate is the shielding effect of electromagnetic waves in decibels (dB):

$$\mathrm{dB} = 20 \log (I_0/I) \tag{2}$$

I_0 = power of the electromagnetic wave irradiated

I = power of the electromagnetic wave transmitted through the sample

Distribution of CuS and Electrical Conductivity. The electrical conductivity (σ) of the CuS–polymer composite film varies with a change in the host-polymer as shown in Figure 1. As for the mechanism of the electric conduction of carbon–polymer and metal–polymer composite, it is recognized[7,9,10] that the electric current flows through a three-dimensional chain or a network of the electrically conducting carbon or metal powders in the composite. If the host–polymer has strong adhesiveness for the surface of the carbon or metal powder, carbon powders or metal powders in the composite will be separated by the insulating host polymer. On the other hand, the electrically conductive chain or network will be formed more easily when the host–polymer has weaker adhesiveness for the carbon or metal powder surface. Thus, in the case of the carbon–polymer composite, a relation between the electrical conductivity and surface energy (surface tension) of the matrix polymer has been determined.[7]

The electrical conduction of the present CuS–polymer composites also seems to be accounted for on the basis of electrically conducting networks formed by the CuS colloidal particles. Scanning electron micrographs (SEM) of the CuS–polymer composites reveal that the diameter (100–150 nm) of the CuS particles is comparable to that (ca. 150 nm) of CuS particles in the original DMF organosols of CuS,[1] indicating that the CuS particles of the organosol do not coagulate strongly during the preparation of the composite film.

To characterize the dispersion state of CuS in the composites, image analysis of SEM photograph was conducted. The section of composite material was prepared by breaking in liquid nitrogen and observing by SEM. The state of dispersion of CuS was characterized by statistical processing using the quadrat method and Morishita's $I\delta$ value.[11] In the quadrant method, the total area of the SEM pattern is divided into small elemental parts of the same area and the number of the points in each element is calculated. It is well known that Morishita's $I\delta$ index is one of the most useful quadrat methods.[11] The index $I\delta$ which plays an important role in the characterization of dispersion of points is given by

$$I\delta = q\delta \tag{3}$$

where

$$\delta = \sum n_i(n_i - 1)/(N(N - 1)) \tag{4}$$

$$N = \sum n_i \tag{5}$$

where N is the total number of particles ($N = \sum n_i$), q is the dividing number, and n_i is the number of particles in

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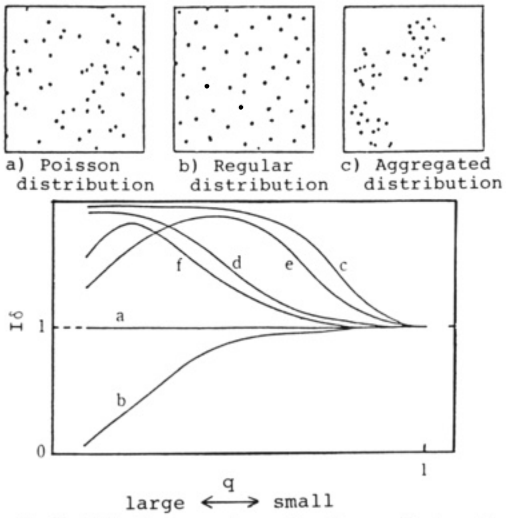

Figure 3. Statistical processing using the quadrat method and Morishta's $I\delta$.[11]

the ith section. Figure 3 shows schematically how q depends on $I\delta$ in each mode of dispersion. For the Poisson distribution all the δ is equal to q^{-1} independent of the value of q, i.e., $I\delta$ is always unity (Figure 3, curve a). Since for Poisson distributions the product of n_i/N and $(n_i - 1)/(N - 1)$ is equal to q^{-1}, δ is the probability to find a particular two point in each element. For the regular mode of distribution, $I\delta$ gradually decreases with increasing q (Figure 3, curve b). For the aggregate distribution, $I\delta$ is larger than unity and increases as the q increases (Figure 3, curves c–f) in regions of relatively small q. The increase in the $I\delta$ value with q is steeper with a larger size of the aggregate; curves c and e in Figure 3 correspond to the aggregate with relatively large size, whereas curves d and f correspond to the aggregate with relatively small size. Furthermore, when the particles are distributed in a regular mode in each aggregate, $I\delta$ has a maximum peak at a certain value of q (curves e and f).

Sumita and co-workers[7b] have applied the statistical pattern processing method proposed by Morishita to the analysis of the dispersion state of carbon powder in carbon–polymer composites and elucidated the difference in the electrical conductivity of the composites depending on the degree of aggregation of the carbon powder; the composite with an aggregated distribution of the carbon powders has the highest electrical conductivity, the composite with randomly distributed carbon powders (Poisson's distribution) has medium electrical conductivity, and the composite with homogeneously distributed carbon powders and with essentially the same distance between the every two carbon particles neighbors has the lowest electrical conductivity. Similar analysis of the present CuS–poly(vinyl alcohol) (PVA), –poly(methyl methacrylate) (PMMA), and –poly(acrylonitrile) (PAN) composites (Figure 1b) by scanning electron micrograph (SEM) reveals the following:

(1) CuS particles in the composite have essentially the same size (o.d. = ca. 150 nm) as the CuS particles in the organosol of CuS.

(2) PMMA containing 5 wt % of CuS has a highly aggregated distribution of CuS particles, whereas PMMA containing 2 wt % of CuS has a more random distribution of CuS particles (cf. Figure 4a,b).

(3) PVA and PMMA, with relatively low surface tensions (37 and 39 dyn cm^{-1}, respectively), give the aggregated distribution of the CuS particles at 20 wt % CuS, whereas PAN, with high surface tension (50 dyn cm^{-1}), affords a homogeneous distribution of the CuS particles at 20 wt % CuS (as for SEM of the PVA composite, see Figure 4c); this agrees with the higher electrical conductivity of the CuS–PVA and –PMMA composites than that of the CuS–PAN composite (Figure 1b). Results of the statistical pattern processing method proposed by Morishita is shown in Figure 5.

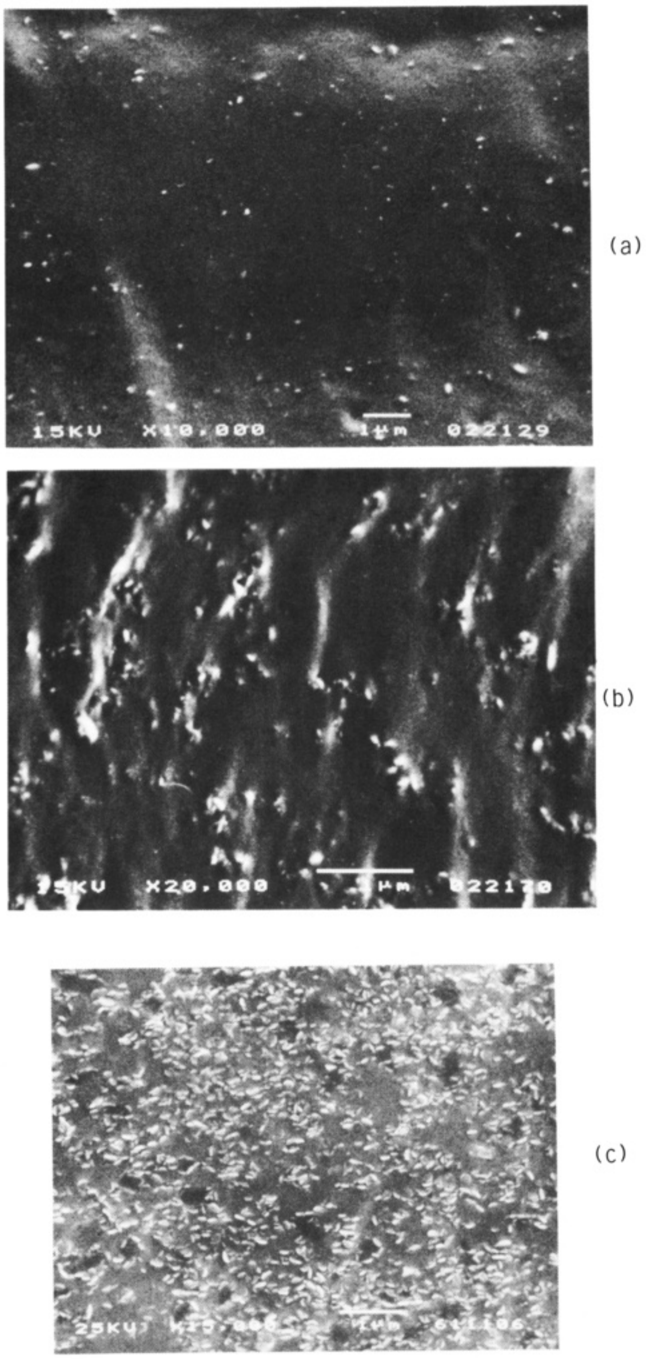

Figure 4. SEM of the CuS–polymer composites. Polymer and wt % of CuS: (a) PMMA, 2%; (b) PMMA, 5%; (c) PVA, 20%.

The CuS–PPA–M–0.8 (20 wt % CuS) with good electrical conductivity (Figure 1c) also shows an aggregated distribution of the CuS particles (Figure 6). These observations suggest that the electrical conductivity of the present CuS–polymer composite is also primarily determined by the distribution state of the CuS particles.

The temperature dependence of the electrical conductivity (σ) of the CuS–polymer composites obeys an Arrhenius type equation:

$$\sigma = \sigma_0 \exp(-E_a/RT) \tag{6}$$

and the activation energies determined for several com-

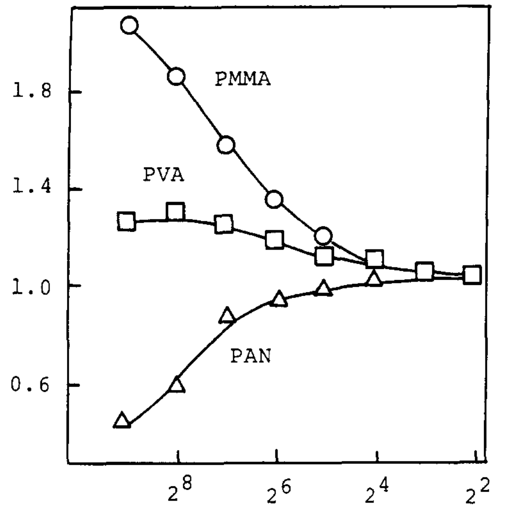

Figure 5. Results of the statistical processing for the CuS–polymer composites (wt % of CuS = 20).

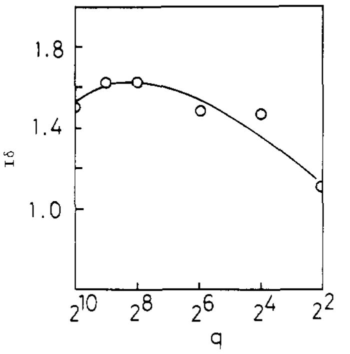

Figure 6. Results of the statistical processing for the CuS–PPA-M-0.8 composite (wt % of CuS = 50).

posites are summarized in Table I. As shown in Table I, the CuS–polymer composite gives a negative activation energy when the content of CuS is high and the electrical conductivity is high, whereas it gives a positive activation energy when the content of CuS is low. Since the electrical conduction in CuS itself shows metallic temperature dependence and gives a negative E_a as previously reported[12] and as is shown in the middle line in Table I, the negative activation energy of the CuS–polymer composite at high CuS content is taken as an indication that the electric current in the composite flows through the network of CuS particles. On the other hand, at a lower content of CuS, the carrier has to pass through the insulating polymer existing between the CuS particles, and this will require a positive activation energy (cf. Table I).

The CuS–polymer composites, in general, show stable electrical conduction over 600 days with a minor decrease of the electrical conductivity under air (10–35 °C with ca. 30–100% humidity). The CuS crystals had a high stability in air.

CdS–Polymer and Other MS–Polymer Composites. Figure 7 shows the dependence of electrical conductivity of the CdS–polymer composite films on the content of CdS in the composites. The composite films were prepared by using DMF organosols of CdS. The electrical conductivity of the composites increases with an increase in the content of CdS. The electrical conductivity of the composites is much lower than that of the CuS–polymer composites owing to the much lower electrical conductivity of CdS.[13]

Table I. Activation Energy (E_a) of the Electric Conduction of the CuS–Polymer and CdS–Polymer Composite Films[a]

polymer	wt % of CuS	E_a, kJ mol^{-1}
For CuS–Polymer Composite		
poly(vinyl alcohol)	31	−5.7
copolymer of vinylidene chloride and acrylonitrile (80:20)	19	2.8
	33	−3.7
poly(vinyl formal)	32	−0.5
poly(acrylonitrile)	32	−0.5
poly(acrylonitrile)	44	−3.7
CuS[b]	100	−11.8
For CdS–Polymer Composite		
poly(vinylidene fluoride)	43	32
poly(vinylidene fluoride)	51	30
copolymer of vinyl chloride and vinyl acetate (90:10)	32	32
	42	28
poly(acrylonitrile)	59	45
poly(vinyl butyral)	44	42
CdS[c]	100	44

[a] Calculated from the Arrhenius type equation (eq 2); temperature range 295–210 K. [b] Measured with a pellet which was prepared by pressing a CuS powder recovered from the CuS organosol at 400 kg cm^{-1}. The pellet shows electrical conductivity of 10^2 S cm^{-1} at 25 °C. [c] CdS pressed pellet, $\sigma = 1.1 \times 10^{-6}$ S cm^{-1} at 25 °C.

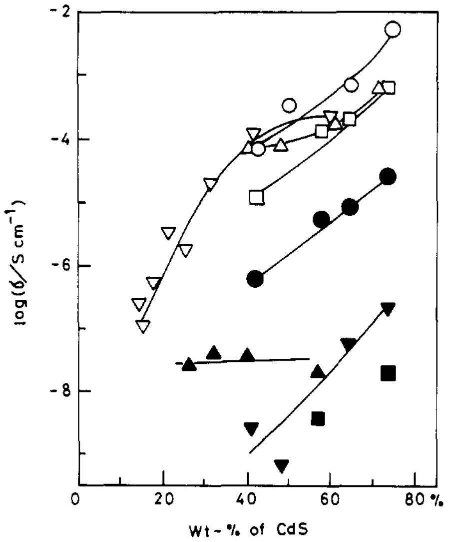

Figure 7. Electrical conductivity of CdS–polymer composites at 25 °C. Polymer: poly(vinylidene fluoride) (○), copolymer of methyl vinyl ether and maleic anhydride (50:50) (△), copolymer of vinyl chloride and vinyl acetate (90:10) (▽), poly(acrylonitrile) (□), poly(vinyl butyral) (●), poly(vinyl formal) (▲), and poly(*N*-vinyl-2-pyrrolidone) (▼). ■: Data for CdS–poly(acrylonitrile) composites prepared by using commercially available CdS powder (see the text).

As shown in Figure 7, the CdS–polymer composite films show electrical conductivities in the range 10^{-4}–$10^{-2.5}$ S cm^{-1}, which are considerably higher than those of previously reported CdS–polymer composites prepared by mixing CdS powder and polymers.[14] Actually, a CdS–poly(acrylonitrile) film prepared by mixing commercially available CdS powder and a DMF solution of poly(acrylonitrile), spreading the mixture on a glass plate, and removing DMF under vacuum showed considerably lower electrical conductivity than that of the present organosol CdS–poly(acrylonitrile) film as shown in Figure 7.

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Table II. Electrical Conductivity of ZnS–, HgS–, NiS–, PdS–, MnS–, and Mixed MS–Poly(acrylonitrile) Composites

no	metal sulfide	wt % of metal sulfide	temp, °C	electrical conductivity (σ), S cm^{-1}	activation energy (E_a), kJ mol^{-1}
1	ZnS	34	20	6.6×10^{-9}	16
2	ZnS	55	20	1.3×10^{-8}	13
3	α-HgS	39	18	3.6×10^{-8}	29
4	α-HgS	56	18	6.5×10^{-8}	26
5	α-HgS	63	18	1.1×10^{-7}	28
6	NiS	14	20	3.5×10^{-6}	11
7	NiS	32	20	1.2×10^{-4}	11
8	PdS	47	25	5.2×10^{-8}	25
9	NnS	42	25	1.0×10^{-9}	*a*
10	$ZnCdS_2$	65	18	1.6×10^{-8}	*a*

[a] Not determined.

The temperature dependence of the electrical conductivity of the CdS–polymer composites also obeys the Arrhenius type equation, eq 6, giving rather large E_a values, which are also included in Table I. SEM analysis of the CdS–polymer composites indicates that the CdS particles have sizes less than 4–5 nm, suggesting that the CdS particles in the organosol[1] do not coagulate with each other during the preparation of the composite film.

Table II summarizes electrical conductivities (σ) of poly(acrylonitrile) composites of other metal sulfides (ZnS, HgS, NiS, etc.) as well as the activation energies (E_a) for electrical conduction. The composites show semiconductivity with values of 10^{-9}–10^{-4} S cm^{-1}, and all of them exhibit positive activation energies. Other polymers, including poly(vinylidene fluoride), poly(methyl methacrylate), and poly(vinyl butyral), afford similar semiconducting composites with ZnS, HgS, NiS, and other metal sulfides. In all cases, the electrical conductivity of the composites increases with an increase in the content of MS. SEM analysis of ZnS–polymer composites indicates that the ZnS particles have sizes of 30–50-nm diameter.

Most of the CdS–polymer composites and other MS–poly(acrylonitrile) composites are stable in air. Among the CdS–polymer composites, those obtained by using poly(vinyl chloride), a copolymer of vinyl chloride and vinyl acetate (90:10), and poly(acrylonitrile) show good mechanical strength.

The electrical conductivities (σ) of the composites shown in Figure 7 and Table II were measured under dry N_2 or Ar. On the other hand, when the composite film was exposed to humid N_2 or N_2-containing alcohol, the electrical conductivities varied. For example, exposure of the ZnS–polymer composites to N_2 containing saturated ethanol vapor at 25 °C leads to an increase in electrical conductivity by a factor of 10^2–10^3. Exposure of a CdS–PPA–TM–1.0 composite to N_2 saturated with water vapor and ethanol vapor at 25 °C also leads to an increase in electrical conductivity by a factor of 10 and 10^2, respectively. On the other hand, exposure of the highly electrically conducting CuS–polymer composites to the vapor of ethanol caused a decrease in electrical conductivity by a factor of 10. The changes in the electrical conductivity by a factor of 10. The changes in the electrical conductivity of ZnS– and CdS–polymer composites with the ethanol and water vapor were reversible. However, in the case of the CuS–polymer composites, their high electrical conductivities were not recovered after removing the vapor of ethanol.

Mode of Electric Conduction and Electric Junction. Hall effect measurements on the CuS–polymer composites and CdS–polymer composites revealed the former is a p-type conductor whereas the latter is an n-type conductor, probably reflecting the type of conduction of the filler.

Table III. Mobility of Carrier for CuS– and CdS–Polymer Composites

MS	polymer	wt % of MS	mobility (μ),[a] cm^2 V^{-1} s^{-1}
CuS	poly(vinyl butyral)	20	50
CuS	copolymer of vinyl acetate and vinyl chloride (10:90)	48	100
CdS	copolymer of vinylidene chloride and acrylonitrile (80:20)	60	−5
CdS	poly(vinyl butyral)	63	−4
CdS	poly(vinylidene fluoride)	63	−17

[a] Sign of the mobility indicates the type of electric conduction: positive for p-type and negative for n-type.

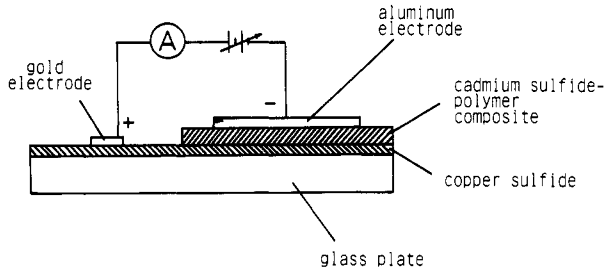

Figure 8. Structure of the heterojunction. Area: 1.2 × 1.2 cm for gold electrode, 1.2 × 2.0 cm for aluminum electrode, and 2.0 × 2.5 cm for cadmium sulfide–polymer composite film. Surface resistance of the copper sulfide substrate film = ca. 100 Ω/square.

CuS[15] itself is usually a p-type conductor, whereas CdS[16] itself is usually an n-type conductor. Both the CuS-polymer and CdS-polymer composites showed relatively large mobilities for the corresponding carriers, which are summarized in Table III.

Since the CuS– and CdS–polymer composites are p- and n-type conductors, respectively, we tried to make electric junctions using the CuS– and CdS–polymer composite films. Formation of an electric junction by pressing the CuS–polymer composite film and the CdS–polymer composite film to each other affords a diode, which shows the expected rectification of electric current. When the CuS–polymer composite film is connected to the plus side and the CdS–polymer composite film is connected to the minus side of a current source, electric current flows smoothly (e.g., 3.5 mA/cm^2 at 4 V). On the other hand, the reverse connection leads to only minor electric current (below 0.1 mA at 4V). However, such p–n junctions were not stable owing to the difficulty of making mechanically good contacts between the two composite films merely by pressing the two films to each other.

Spreading of the organosol containing metal sulfide and polymer on electrically conducting substrates and removal of solvent (painting method) afforded mechanically good contacts when appropriate polymers such as poly(vinyl butyral), poly(vinylidene fluoride), and copolymers of vinyl chloride were selected, and the MS–polymer composite adhered well against the electrically conducting substrates. Figure 8 shows the structure of the heterojunction thus prepared by spreading a DMF organosol containing CdS (ca. 0.1 mol dm^{-3}) and poly(vinyl butyral) on a copper sulfide substrate[5a] formed on the surface of a glass plate; the copper sulfide substrate is considered to be a p-type conductor.[5] Kinds of host–polymers and weights percent of CdS in the composites are shown in Table IV.

When an 80:20 copolymer of vinylidene chloride and acrylonitrile is used as the polymer to form the composite

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(15) Rao, C. N. R.; Pisharody, K. P. R. *Progr. Solid State Chem.* **1975**, *10*, 207.

(16) For example: Boer, K. W. *Phys. Status Solidi a* **1981**, *66*, 11.

Table IV. Rectification of Heterojunction

no.	p-side[c]	n-side[c]	rectification ratio[a]
1[b]	copper sulfide on glass plate	CdS–polymer (80:20 copolymer of vinylidene chloride and acrylonitrile) composite (wt % of CdS = 60)	44
1[b]	copper sulfide on glass plate	CdS–poly(vinyl butyral) composite (wt % of CdS = 63)	30
3[b]	copper sulfide on glass plate	CdS–poly(vinylidene fluoride) composite (wt % of CdS = 63)	102
4	CuS-polymer (10:90 copolymer of vinyl acetate and vinyl chloride) composite (wt % of CuS = 48)	n-Si (single-crystal plate)	30

[a] I(at V = +5 V)/I(at V = −5 V). [b] For heterojunction shown in Figure 8. [c] For the mobility of carrier of the composite, see Table III.

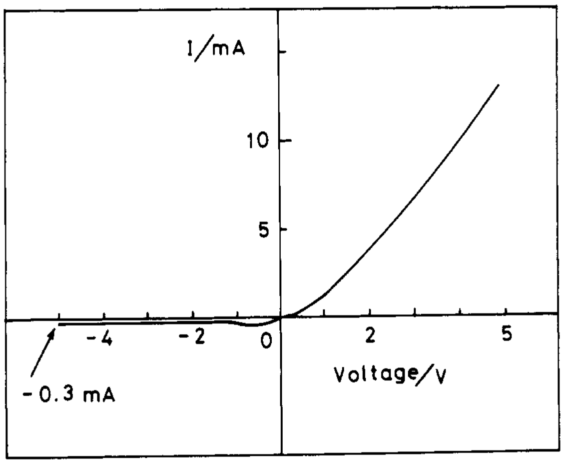

Figure 9. I–V characteristic of the heterojunction shown in Figure 8. Polymer = 80:20 copolymer of vinylidene chloride and acrylonitrile; wt % of CdS = 60; at room temperature (ca. 25 °C).

film (wt % of CdS = 60; thickness of film = 10 μm), the heterojunction gives the I–V curve shown in Figure 9. The composite film shows an electrical conductivity of ca. 1 × 10^{-5} S cm^{-1} and an electron mobility of 5 cm^2 V^{-1} s^{-1} (Table III). Both the electric junction between Al– and the CdS–polymer composite and that between Au and the copper sulfide substrate in Figure 8 were ohmic. The origin of a small increase in the current observed at about −0.7 V in the I–V curve (Figure 9) has not been clarified.

As shown in Figure 9, when the copper sulfide substrate is connected to the plus side, electric current flows smoothly. However, in the reverse connection, the flow of only a minor electric current is observed. The rectification ratio estimated from the electric current at V = +5 V (I = 13.25 or 2.65 mA cm^{-2}) and at V = −5 V (I = 0.3 mA cm^{-2}) is 44.

The use of other CdS–polymer composites gives similar rectification curves. Rectification ratios estimated as described above are listed in Table IV. Table IV also includes data for a heterojunction between CuS–polymer composite film and n-Si; the heterojunction (no. 4 in Table IV) was prepared by spreading the organosol containing CuS and polymer on an n-Si plate followed by removal of the solvent.

Conclusion

Organosols of MS (M = Cu, Cd, Zn, etc.) are useful as starting materials to prepare electrically conducting MS–polymer composite films. Organosols of CuS especially afford the composite films with the highest electrical conductivity (as high as 50 S cm^{-1}), which cannot be attained by the usual mixing of CuS powder and polymer. CuS–poly(parabanic acid) composite films have excellent mechanical and thermal properties.

The electric current is considered to flow through the network of MS particles as judged from activation energies for the electric conduction, SEM analysis, and type (p or n) of the electric conduction. The CuS–polymer and CdS–polymer composite films are p-type and n-type conductors, respectively, and heterojunctions, which show rectification effects, can be prepared by using the composite films.

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Registry No. PVA, 9002-89-5; PVf, 25068-14-8; PAN, 25014-41-9; PVF, 24937-79-9; PPA, 60092-26-4; CuS, 1317-40-4; CdS, 1306-23-6; ZnS, 1314-98-3; HgS, 1344-48-5; NiS, 16812-54-7; PdS, 12125-22-3; MnS, 18820-29-6; $ZnCdS_2$, 39466-56-3; vinylidene chloride–acrylonitrile copolymer, 9010-76-8; vinylidene chloride–vinyl acetate copolymer, 26781-55-5.