

Introduction of Cu(II) Complex into Transparent Synthetic Resin and Optical Function of the Resin as a Near-Infrared Ray Cutoff Filter

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ABSTRACT: A mole ratio method was conducted to determine a necessary condition to solubilize Cu(II) ion into an organic solvent. Copper benzoate anhydrous (CB) and acetone was used as a Cu(II) ion supplier and a solvent, respectively. Methacryloyloxyethyl phosphate (PMOE) and di(2-ethylhexyl) phosphate (DIEHP) were used as ligands for solubilization. Cu(II) ion was solubilized with only two PMOE molecules, although six molecules were needed for DIEHP. PMOE formed an intermediate layer which surrounded the Cu(II) ion with two molecules between the ion and solvent and made it possible to solubilize Cu(II) ion into the organic solvent. In the case of DIEHP, however, six molecules were needed to form such a layer for solubilization. Furthermore, Cu(II) ion was introduced homogeneously into poly(methyl methacrylate) (PMMA) by copolymerization of PMOE with MMA, although the polymer was opaque in the case of DIEHP. The ligand having a methacryloyl group was considered to participate in the polymerization process, which avoided exclusion of the Cu(II) complex from polymer phase. The intermediate zone formed by PMOE was considered to keep compatibility of Cu(II) ion with the polymer matrix even after polymerization. The near-infrared ray cutting-off filter made of resin was realized by introducing Cu(II) ion at higher concentration through complexation with the proper ligand. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 903–912, 1998

Key words: Cu(II) complex; phosphoric acid ester; solubility; near-infrared ray; optical filter

INTRODUCTION

The near-infrared (NIR) ray cutting-off filter is an indispensable optical device for the correction of luminoefficiency for silicon photo diode (SPD) and charge coupled device (CCD) because SPD and CCD respond to needless rays in NIR region.¹ They need a luminoefficiency filter to confine their light response to the range of human luminosity.

However, in spite of large demands, an NIR ray cutoff filter made of synthetic resin had not been realized.

We took note of Cu(II) ion as being a metal ion having an optical function of cutting off NIR ray. We had already noticed by preliminary experiment that the Cu(II) ion has broad light absorption from 700 to 1500 nm, showing a peak at around 800 nm, in which case the ion forms a complex with a phosphate group and the optical feature is suitable for the photometric filter. There is no substance having such a suitable optical feature which surpasses the Cu(II) ion. Although dye for NIR ray absorption is easily purchased, the absorbing wavelength range is much nar-

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rower than that of Cu(II) ion, and the absorbance is not enough for the application to CCD and SPD. In addition, the organic absorbing dye is apt to deteriorate by the light and it may cause trouble in the exposure system and color balance system of the instruments. The dye, therefore, is not suitable for the optical filter to such application. The introduction of the Cu(II) ion is unavoidable in order to realize a practical NIR ray cutoff filter.

Solubilizing metal ion into polymer at a concentration high enough for actual use is not easy. We started by investigating the solubilizing phenomena of metal ion into organic solvent. First, selection of ligand for solubilization, complex solubility, number of coordination, and the necessary conditions of solubilization into organic solvent were discussed. Then, the method of how to introduce Cu(II) complex homogeneously into polymer matrix at a higher concentration was discussed, comparing different types of ligand.

EXPERIMENTALS

Materials

Copper benzoate anhydrous (CB) in the first grade was obtained from Kanto Chemical Co. Phosphoric acid di(2-ethylhexyl) ester (DIEHP) was purchased from Tokyo Kasei Co. Phosphoric acid methacryloyloxyethyl ester (PMOE) was purchased from Kyoeisya Kagaku Co. Acetone was the first grade product purchased from Kanto Chemical Co. Methyl methacrylate (MMA) was purchased from Kurare Co. All chemical reagents were used without any purification.

Mole Ratio Method

Acetone, CB, and phosphoric acid esters were used as a solvent, a Cu(II) ion supplier, and ligands for solubilization, respectively. A fixed amount of CB, 0.0612 g, was mixed in a fixed amount of acetone, 10 g, and then the ligands were added into the acetone-CB mixture. The solubility of CB or its products was observed. The amounts of the ligands are shown in Tables I and III. The sample solutions were stirred at room temperature, approximately 23°C, for 6 h. The $[\text{OH}]/[\text{Cu}^{2+}]$ mole ratio, in which OH means the same as the POH group of ligand, was used as a parameter which means quantitative balance between Cu(II) ion and ligand. The relationships between solubility, peak wavelength, peak ab-

sorbance, and $[\text{OH}]/[\text{Cu}^{2+}]$ value were observed, in relation to each other.

Measurement of Ultraviolet/Visible/NIR Spectra

The spectra of ultraviolet (UV), visible (VIS) and NIR ranges were measured with a UV/VIS/NIR spectrophotometer U-4000 produced by Hitachi Co. The sample solutions prepared for the mole ratio method were poured into a quartz cell with a 10-mm light path length, and their absorbance or transmittance was measured from 330 to 1500 nm. The samples having insoluble solute and precipitant were measured after filtration. The polymerized plates were measured without any treatment.

Synthesis of Optical Filter

MMA (10 g), CB (0.612 g), and specific amount of ligands were mixed, and CB was solubilized completely at room temperature. After addition of *t*-butyl peroxyoctanoate used as an initiator, the monomer solutions were polymerized. The compositions of the monomer solutions are shown in Table IV. The monomer mixtures were poured into molds for plates with 10 mm thickness and polymerized in a oven at 60°C for 15 h and then at 80°C for 3 h. Optical features were observed by measuring absorption and transmittance.

RESULTS AND DISCUSSION

Necessary Condition for Solubilization of Cu(II) Ion

A mole ratio method which utilizes the drastic change in solubility of metal ion into solvent accompanied by ligand substitution is available to determine number of ligands and coordination state of the complex and also to speculate the necessary conditions for solubilization of metal ion into a solvent. Concerning the method, we have previously reported about solubilization phenomena of CB in MMA.² In the report, a necessary condition for solubilizing CB into MMA and PMMA was determined by the method utilizing the drastic change in solubility of CB. This time, phosphoric acid esters were selected as ligands because the optical characteristics of the Cu(II) complex formed with the phosphate were suitable for the NIR cutoff filter aimed at actual use.

In the experiments, a simple combination of

Table I Data of Mole Ratio Method for DIEHP Series

Code	[OH]/[Cu ²⁺]	DIEHP (g)	Solubility	λ_{\max}	Abs
1	1	0.0645	PS	728	0.4155
2	2	0.1291	PS	736	0.2869
3	3	0.1936	PS	798	0.1421
4	4	0.2582	PS	810	0.2405
5	5	0.3227	PS	820	0.4336
6	6	0.3872	S	818	0.5144
7	7	0.4515	S	826	0.5002
8	8	0.5164	S	828	0.4988

PS, partially soluble; S, completely soluble; Abs, absorbance at λ_{\max} .

solvent, solute, and ligand was adopted to determine the necessary conditions for Cu(II) ion solubilization, i.e., acetone as a solvent, CB as a Cu(II) ion supplier, and DIEHP as a ligand for solubilization. Cu(II) ion is apt to bind DIEHP rather than benzoic acid, and, therefore, ligand replacement reaction by DIEHP easily occurs. The DIEHP was chosen as an analogue for PMOE because the molecular weight of DIEHP ($M_w = 322.43$ g/mol) is almost the same as that of PMOE diester ($M_w = 322.28$ g/mol). The chemical formulas of the ligands are shown in Figure 1.

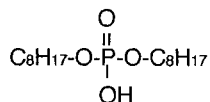
The results of the mole ratio method of the DIEHP series are shown in Table I. Concerning CB solubility, it showed a boundary point at $[\text{OH}]/[\text{Cu}^{2+}] = 6$, divided into two categories, i.e., partially soluble at less than 6 and completely soluble at 6 or more. Although precipitate was

separated from solution, it was not removable from filter paper. Therefore, quantitative detection of solubility from residual precipitate was not possible in this experiment.

The UV/VIS/NIR absorption spectra are shown in Figure 2. The peak wavelength and absorbance are shown in Table I. The relationships between the peak wavelength, the peak absorbance, and $[\text{OH}]/[\text{Cu}^{2+}]$ are summarized in Figure 3. The peak wavelength shifted from 730 to 830 nm with the increase in $[\text{OH}]/[\text{Cu}^{2+}]$.

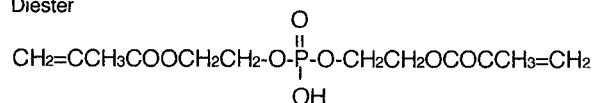
At less than 3 in the $[\text{OH}]/[\text{Cu}^{2+}]$, the peak absorbance decreased with increasing $[\text{OH}]/[\text{Cu}^{2+}]$, although they were definitely high in spite of low solubility. The peak wavelength was extremely low compared with that of other samples. In the range of 3 to 6, the peak wavelength and absorbance proportionally increased with the increase in $[\text{OH}]/[\text{Cu}^{2+}]$. In the range $[\text{OH}]/$

Phosphoric acid di(2-ethylhexyl) ester (DIEHP)



Mixture of mono- and di- esters of phosphoric acid methacryloyloxyethyl ester (PMOE)

Diester



Monoester

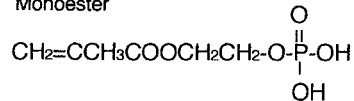


Figure 1 Chemical formulas of ligands for complexation to Cu(II) ion.

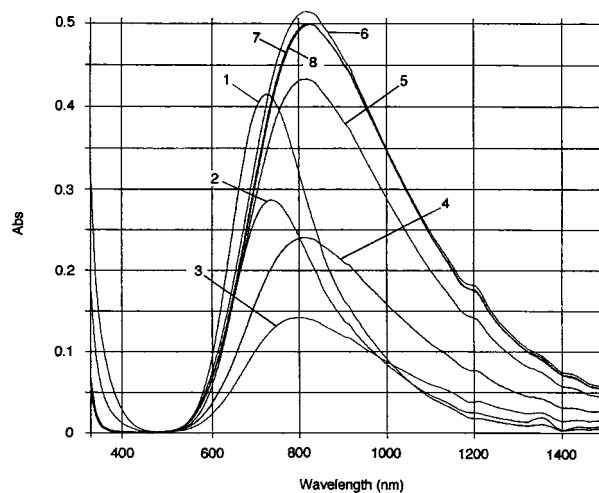


Figure 2 UV/VIS/NIR absorption spectra of samples of DIEHP series. Light pass length, 10 mm.

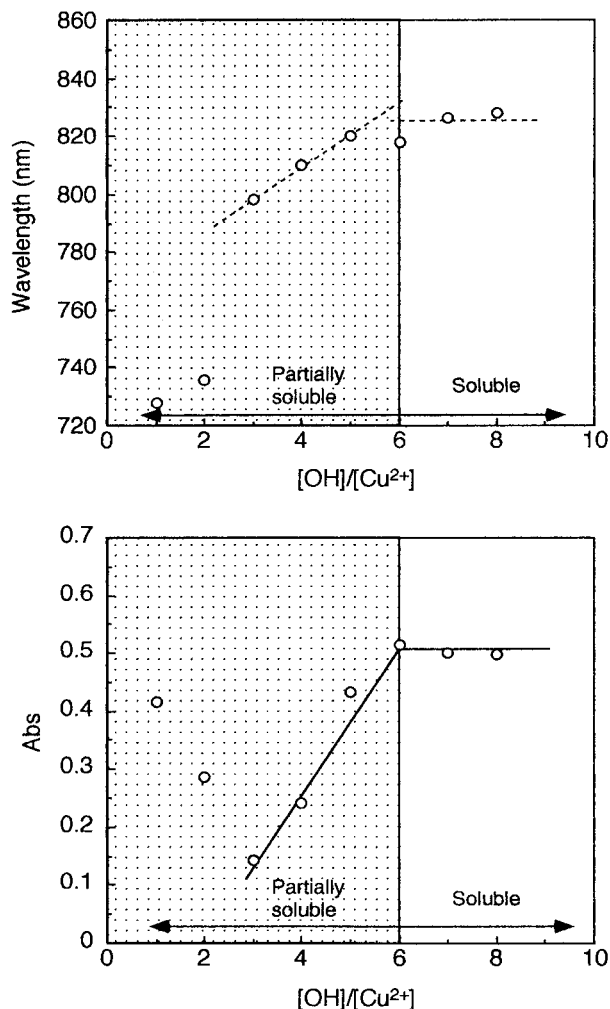


Figure 3 Dependence of peak wavelength, peak absorbance, and solubility of CB on $[\text{OH}]/[\text{Cu}^{2+}]$ value for DIEHP series.

$[\text{Cu}^{2+}] \geq 6$, a remarkable change was not recognized.

CB inherently forms dimeric structure, and its peak absorbance appears at 660 nm.²⁻⁵ Generally, salts obtained from Cu(II) ion and carboxylic acid form dimeric structure,^{5,6} and the structure changes to monomeric structure in some conditions,⁶⁻¹⁰ which demonstrates a broader absorption peak than that of dimeric complex at wavelengths higher than 660 nm. In this experiment, although the counter ion was not a carboxyl group, the complex with the $[\text{OH}]/[\text{Cu}^{2+}] = 6$ showed a very broad peak at 830 nm, which implies that the complex was a monomeric structure. The intermediate product between dimer and monomer was considered to be formed at the intermediate value from 1 to 6, which resulted in

the peak shift from 660 to 830 nm with the change in $[\text{OH}]/[\text{Cu}^{2+}]$.

The peak wavelength changed drastically between 2 and 3 in $[\text{OH}]/[\text{Cu}^{2+}]$, and the dependence of absorbance on $[\text{OH}]/[\text{Cu}^{2+}]$ altered from negative slope to positive slope at around 3. At less than 3, the structure of the solubilized copper compound was considered to keep the dimeric structure because the spectra suggested the features of dimer, i.e., narrower peak at around 700 nm. Although the extinction coefficient of CB in acetone was not obtained in this research, we have ascertained that its extinction coefficient at the peak is more than five times that for the complex solubilized by phosphate ligands.¹¹ Therefore, a slight or intermediate amount of CB could show a larger absorbance than that of the product. Further, the result that the absorbance decreased with increasing $[\text{OH}]/[\text{Cu}^{2+}]$ meant that the solubilized substance in this range was not product but intermediates which should be consumed to produce the final product. The solubilized substances in the range $[\text{OH}]/[\text{Cu}^{2+}] < 3$ seemed to have dimeric structure formed with both benzoic acid and DIEHP at the initial stage of ligand substitution, and they were barely soluble.

In the range 3 to 6 in $[\text{OH}]/[\text{Cu}^{2+}]$, however, a peak appeared at around 800 nm, which suggested monomeric structure. The absorbance increased with an increase in $[\text{OH}]/[\text{Cu}^{2+}]$, which meant that the solubilized compound was the intermediate product that was solubilized through complexation with DIEHP.

The complex in a range of $[\text{OH}]/[\text{Cu}^{2+}] \geq 6$ was considered to be the final product after sufficient substitution reaction and coordination by DIEHP and to be the stable complex formed with six DIEHP molecules. This meant, in other words, that the substitution and coordination were saturated at 6 in $[\text{OH}]/[\text{Cu}^{2+}]$ and excessive DIEHP molecules did not cause any influence on the complex.

The results discussed above suggested that the solubilization of Cu(II) ion into acetone was attained with six molecules of DIEHP, which meant that two DIEHP molecules as counter ions and four molecules as coordination ligands were required. Six such DIEHP molecules binding at the Cu(II) ion seemed to surround the Cu(II) ion.

Kato et al. reported about solubilization of metal compounds in organic solvent and also mentioned the surrounding structure.⁴ They explained that solubilization into organic solvent was succeeded by the coordination or interaction

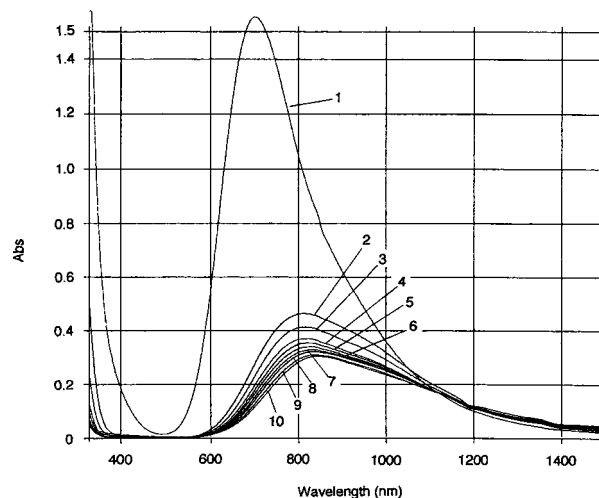
Table II Composition of PMOE

Parameter	Diester	Monoester
Molecular weight (g/mol)	322.28	210.14
Weight percent	62.5	37.5
Mole percent	52.0	48.0

of solvent molecules at empty coordination sites of metal compound and also by surrounding metal ion, with the intermediate layer formed by the counter ion and interacting solvent molecule between metal ion and organic atmosphere. It seemed in this study that acetone molecules could not interact with CB or Cu(II) ion, DIEHP could bind through an ionic bond, and four additional DIEHP molecules could bind to Cu(II) ion even after replacement of counter ions. The results suggest that the necessary condition for solubilization of Cu(II) ion was $[\text{OH}]/[\text{Cu}^{2+}] \geq 6$, satisfying the conditions as follows: (1) forming six coordination complexes; (2) surrounding Cu(II) ion completely to form an intermediate layer between the ion and the organic solvent.

Structure and Coordination Number of the Cu(II) Complex Formed with PMOE

PMOE is a phosphoric acid ester containing a methacryloyl group in its structure; it was chosen as a polymerizable ligand with comonomers for optical filter matrix. The PMOE is an equimolar mixture of monoester and diester as a result of the reaction process of raw materials, P_2O_5 and 2-hydroxyethyl methacrylate. Although pure diester reagent was better for our experiments, we had no choice but to use the mixture of diester

**Figure 4** UV/VIS/NIR absorption spectra of samples of PMOE series. Light pass length, 10 mm.

and monoester because it was hard to obtain a pure one. The chemical structure is shown in Figure 1, and the composition of diester and monoester is shown in Table II. The $[\text{OH}]/[\text{Cu}^{2+}]$ value was also used as a parameter to express the mole balance of PMOE and Cu(II) ion and was calculated from the analytical data shown in Table II.

The results of the mole ratio method for the PMOE series are shown in Table III. The UV/VIS/NIR absorption spectra are shown in Figure 4. The relationships between absorption peak wavelength, peak absorbance, and $[\text{OH}]/[\text{Cu}^{2+}]$ value are shown in Figure 5. CB was solubilized completely at 2 or more in the $[\text{OH}]/[\text{Cu}^{2+}]$. The peak wavelength and the peak absorbance changed extremely in a range less than 2, while they showed approximately constant value at 2 or more.

Table III Data of Mole Ratio Method for PMOE Series

Code	$[\text{OH}]/[\text{Cu}^{2+}]$	PMOE (g)	Solubility	λ_{max}	Abs
1	1	0.0363	PS	700	1.5536
2	2	0.0726	S	810	0.4653
3	3	0.1089	S	814	0.4141
4	4	0.1452	S	824	0.3709
5	5	0.1815	S	824	0.3550
6	6	0.2177	S	826	0.3411
7	7	0.2540	S	840	0.3290
8	8	0.2903	S	838	0.3239
9	9	0.3266	S	838	0.3108
10	10	0.3629	S	840	0.3047

PS, partially soluble; S, completely soluble; Abs, absorbance at λ_{max} .

The important thing in this report is that the Cu(II) ion was completely solubilized at 2 in $[\text{OH}]/[\text{Cu}^{2+}]$ for the PMOE series. This means that the Cu(II) ion could be solubilized only by replacing counter ions. In the section about DIEHP, it was speculated that the Cu(II) ion should be surrounded by an intermediate layer formed between Cu(II) ion and acetone for solubilization. Referring to the solubilization condition in the case of the DIEHP series, the results of the PMOE series imply that the PMOE could surround the Cu(II) ion with only two molecules and also satisfy the six coordinations.

In this study, the solubilization phenomena were explained by the model using only diester to simplify the interpretation, although it was diffi-

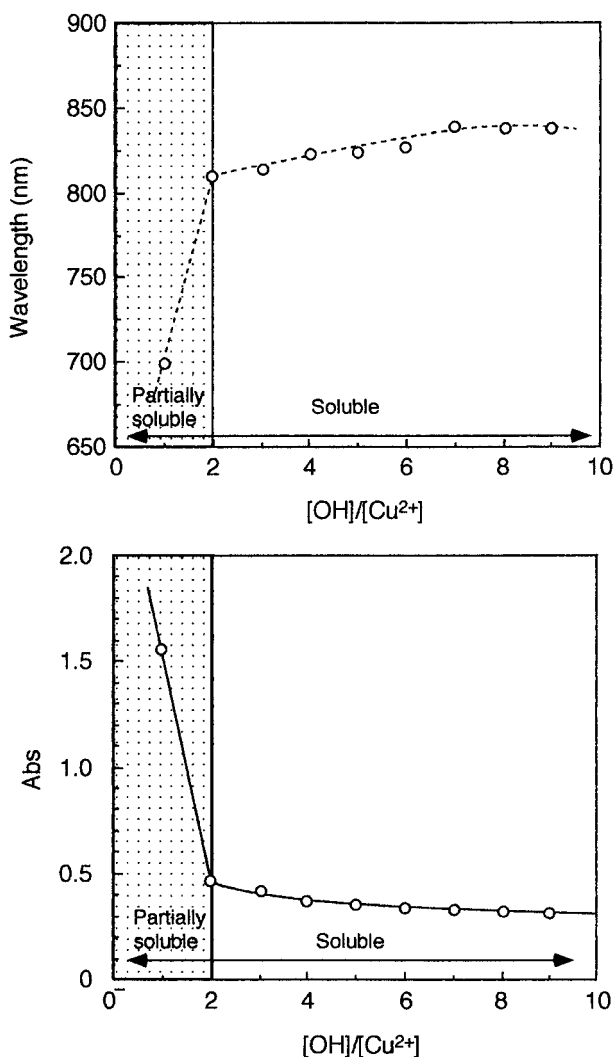


Figure 5 Dependence of peak wavelength, peak absorbance, and solubility of CB on $[\text{OH}]/[\text{Cu}^{2+}]$ value for PMOE series.

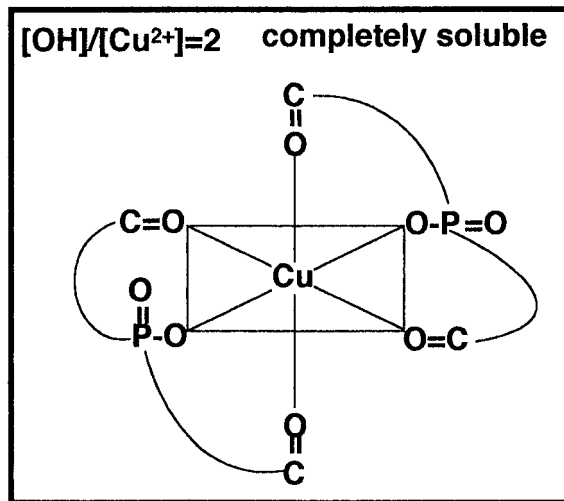
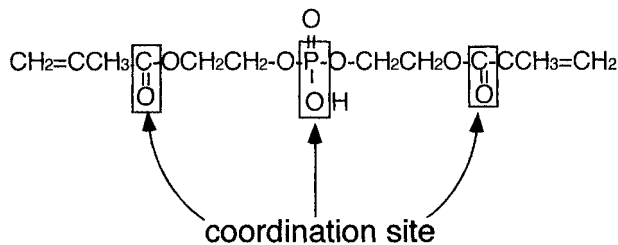


Figure 6 Structures of the PMOE and the Cu(II) ion complex with the two PMOE molecules.

cult to speculate the composition, structure, and coordination state of the Cu(II) complex, because the PMOE was a mixture of monoester and diester. The solubilization seemed to occur mainly because of the complexation with diester in PMOE, because in the case that only monoester was used, the product after ligand substitution reaction was insoluble. Here, the solubilization phenomenon of Cu(II) complex with PMOE at a $[\text{OH}]/[\text{Cu}^{2+}]$ value of 2 can be explained reasonably by assuming that PMOE had plural coordination sites to the Cu(II) ion, namely, it was a polydentate ligand. The PMOE molecule's chemical formula was comprised with the phosphoric acid group and the methacryloyl group linked by the ethyleneoxyde, as shown in Figure 6. The methacryloyl group has a C=O group, which was considered to be a candidate for the coordination to the Cu(II) ion. With the assumption that the oxygen atom of C=O could have coordinated to the Cu(II) ion, the diester of PMOE could include three coordination sites in one molecule, as shown in Figure 6. The simple coordination model in Figure 6 was considered arbitrarily to satisfy the six coordinations with two PMOE molecules.

Compared with the diester model of PMOE, the complex formed only with the monoesters was not soluble at all. Cu(II) ion and the monoesters probably formed a polymer-like structure in which Cu(II) ion and the monoesters were linked reciprocally by ion binding. The elemental analysis data of the precipitate showed an equimolar ratio for P and Cu(II) ions, which led to the speculation of polymer formation by the Cu(II) ions and the monoesters. These results suggest that the pure diester reagents are desirable for ideal complexation and for ideal solubilization.

Further, to check the ability of coordination of the C=O group to Cu(II) ion, a solubility test was conducted by using MMA as a ligand having the C=O group and DIEHP as a phosphate ligand. Referring to the discussion of the DIEHP series, if the C=O group had an ability enough to coordinate, two molecules of DIEHP as counter ions and four MMA molecules as coordination ligands would be needed for solubilization. The experiment was conducted using acetone as a solvent. However, we could not recognize the effect of adding MMA as a ligand for solubilization.

The comparison between the cases of PMOE and MMA showed the differences in the ability of the methacryloyl group to coordinate, and these results implied predominance of the polydentate ligand which forms chelate structure. The C=O of PMOE was located near the Cu(II) ion because the mobility of the group was confined at around the Cu(II) ion by ion binding between PO^- and Cu(II). An attractive force of MMA to Cu(II) ion, however, was too weak to bind, and the mobility of MMA molecule without confinements made it no longer possible for the C=O group to interact with the Cu(II) ion.

Concerning the light absorption, all samples at 2 or more in $[\text{OH}]/[\text{Cu}^{2+}]$ value showed the absorption peaks at more than 810 nm with broad wavelength dependence. The chelate structure seemed to stabilize monomeric structure at the lower $[\text{OH}]/[\text{Cu}^{2+}]$ value.

Here, we have to think about the complexes formed with the mixture of monoesters and dies-

ters of PMOE. Because the complexes formed with pure monoester are insoluble, as mentioned above, the presence of the diester probably made it possible to solubilize the Cu(II) ion complex. The Cu(II) ion and the monoester formed an oligomeric complex to some degree, and the oligomeric complex partially contained diesters which solubilized the complexes. Therefore, the complex structure is considered to be not as simple as the one shown in Figure 6. However, we certainly considered that coordinating PMOE molecules surrounded the Cu(II) ions and formed an intermediate layer between the ion and acetone.

Synthesis of Cu(II) Ion-Containing Monomer

The Cu(II) complexes mentioned above were solubilized in MMA, and the solutions were polymerized through the procedure written in the experimental section. The compositions of monomer solutions are shown in Table IV. The amount of CB was fixed to compare the optical feature, and the amounts of ligands for each samples were determined based on the boundary point mentioned above, namely, 6 for the DIEHP and 2 for the PMOE in $[\text{OH}]/[\text{Cu}^{2+}]$. The DIEHP was used as an unpolymerizable ligand, and the PMOE was used as a polymerizable one.

The polymer disc including the Cu(II) complex formed with DIEHP was opaque. The polymer disc plate containing the Cu(II) ion-PMOE complex, however, was obviously transparent.

The difference in transparency was very important for the discussion about Cu(II) ion complex solubility into polymer. The difference in solubility was considered to result from the difference in the properties of the ligand, especially whether the ligand had a polymerizable functional group.

In the case of DIEHP, the solubility of the complex was presumably lowered with the increase in the molecular weight of PMMA in the propagation process, and the complex was excluded from the polymer phase, resulting in phase separation. In the case of PMOE, however, the methacryloyl

Table IV Monomer Compositions for NIR Ray Cutoff Filter

Sample No.	CB	MMA	DIEHP	PMOE	$[\text{OH}]/[\text{Cu}^{2+}]$	Solubility in Monomer	Solubility in Polymer
1	0.612	10.00	3.869	0	6	Soluble	Phase separation
2	0.612	10.00	0	0.7264	2	Soluble	Soluble

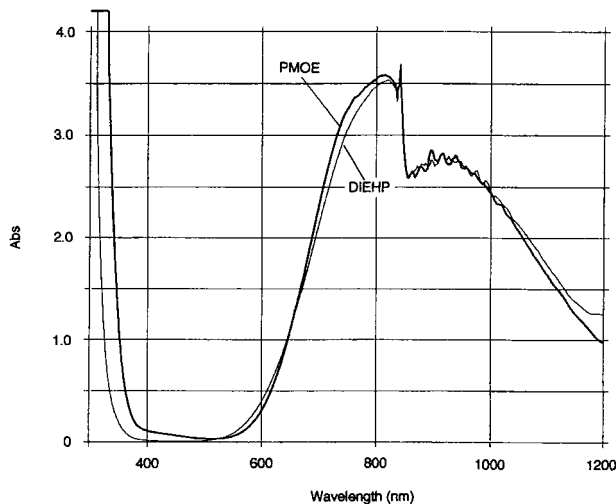


Figure 7 UV/VIS/NIR absorption spectra of monomer solutions containing Cu(II) ion complexes formed with DIEHP and with PMOE. Light pass length, 10 mm.

group of the ligand could participate in the polymerization process of MMA and the complexes having the polymerizable group were easily introduced into polymer chains and matrix. The key point to obtaining a transparent plate is considered to be the adoption of the ligand having a radical polymerizable functional group.

In this study, although DIEHP and PMOE were used as unpolymerizable and polymerizable ligands, respectively, most ligands can be classified into two categories, namely, unpolymerizable and polymerizable. It was hard to introduce Cu(II) complex with unpolymerizable ligand into polymer, even if the ligand structure was designed thoroughly. By using polymerizable ligand, however, the complex introduction was much easier, regardless of ligand structure and molecular weight. The classification substantiated the importance of the use of the ligand containing a polymerizable group for metal ion incorporation into polymer matrix at a high concentration.

Optical Feature of the Cu(II) Ion in Monomer and Polymer

The absorption spectra of the monomer samples prepared for optical filters are shown in Figure 7. Although a quantitative discussion cannot be done because the Cu(II) ion concentration was too high to measure the absorbance correctly, the absorption for both complexes showed peaks at around 800 nm and the wavelength dependence

of the absorbance was essentially almost the same. The appearance of the peak at around 800 nm and broad absorption meant that the Cu(II) ion complex solubilized in MMA had monomeric structure.

The transmittances of the monomer solutions are shown in Figure 8. The transmittance ($T\%$) in the range from 700 to 1200 nm was almost zero. That in the ultraviolet (UV) region was also almost zero. The absorption in the UV light range was considered to be attributed to the charge transfer between Cu(II) ion and oxygen atom, which is generally a known phenomenon.¹²⁻¹⁴ The high transparency, however, was recognized in the VIS range.

The absorption and transmittance spectra of the transparent polymerized filter containing the PMOE-Cu(II) complex are shown in Figure 9. The peak appearance at 800 nm with broad wavelength dependence could result in the speculation of the formation of a monomeric complex structure.

The transmittance in the UV and NIR regions was almost zero, and this filter passed only visible light. Because the absorption and transmittance spectra were essentially almost the same as those of monomer, the structure and coordination state of the Cu(II) complex in the monomer was considered to be kept through polymerization and also in polymer matrix.

Although it is difficult now to speculate precisely the complex structure in the solubilized state because the obtainable data at this time are

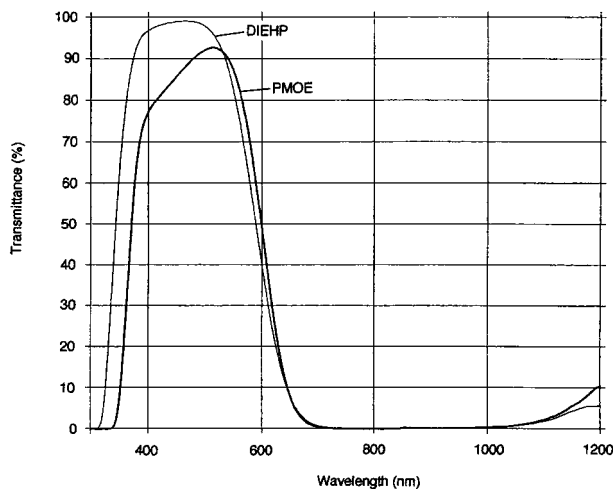


Figure 8 UV/VIS/NIR transmittance spectra of monomer solutions containing Cu(II) ion complexes formed with DIEHP and with PMOE. Light pass length, 10 mm.

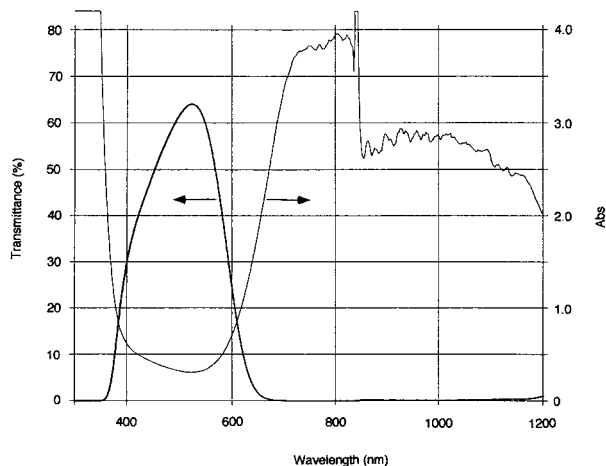


Figure 9 UV/VIS/NIR transmittance and absorption spectra of the plastic filter containing Cu(II) ion complexes formed with PMOE. Thickness, 10 mm.

the solubility of the complex and the UV/VIS/NIR spectra, the complex in polymer is thought to be solubilized in the state as shown in Figure 10. Cu(II) ion was surrounded by both of the two oxygen atoms of the phosphate group bonding through the ion bonding and the four oxygen atoms of the carbonyl group binding through the coordination, which form an intermediate layer between the metal ion and the polymer matrix. Further, because the layer itself was a part of the polymer matrix, the complex could be introduced without exclusive or repulsive force. This layer formation is considered to make it possible to solubilize Cu(II) ion into polymer at a higher concen-

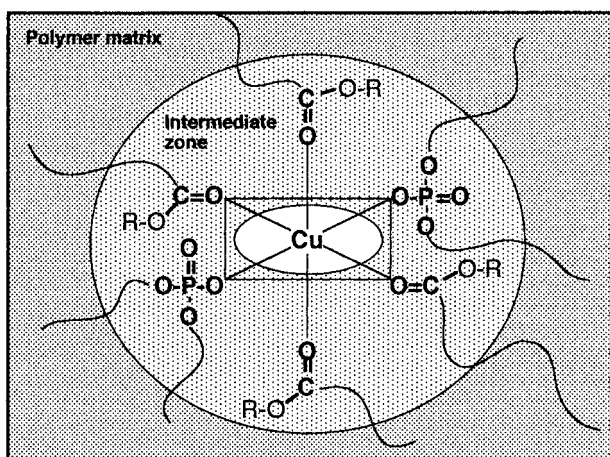


Figure 10 The model structure of Cu(II) ion complex in solubilized state in the polymer matrix.

tration. Now we can solubilize Cu(II) ion by about 15 wt % into acrylate-based resin by improving the method described in this article.

Finally, we would like to briefly introduce the needs and applications of the NIR ray cutoff filter because it is probably helpful to understand this research. The character of this filter that cuts off UV and NIR light and passes through only VIS light is similar to the wavelength dependence of light response of the human optic cell. This optical feature is available to confine the light response of CCD and SPD to the VIS range.

The SPD and CCD are the devices which translate an optical signal to an electric signal, and the devices have a light response in the range from 300 to 1000 nm. The wide-range light response, which includes unneeded ray, causes the trouble for light exposure and color balance. For the working of these devices, the light response should be confined to the visible range. Therefore, a UV and NIR cutoff filter is an indispensable optical device for SPD and CCD. The substance that can effectively cut the UV and NIR ray is the Cu(II) ion.

We have realized and commercialized the UV/NIR cutoff filter made of synthetic resin for practical use, which has been the first product made of synthetic resin in the world, by intensive research of the method for Cu(II) ion introduction based on this study, and have realized a thinner filter, e.g., 0.5 mm, which has enough NIR cutoff function to actually use. The UV/VIS/NIR spectrum of one of the commodity samples containing 8.0 wt % Cu(II) ion is shown in Figure 11 as an exam-

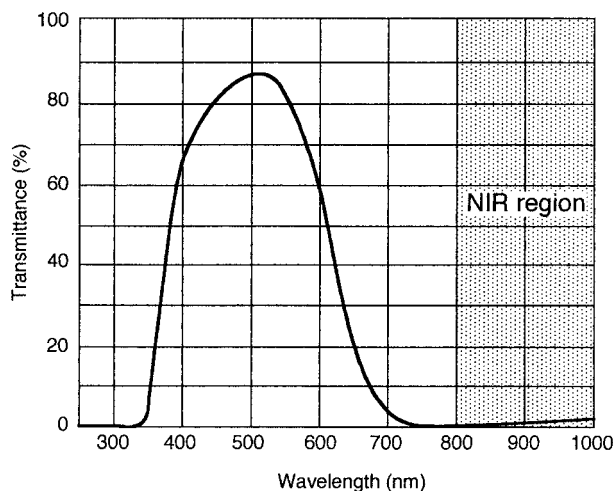


Figure 11 Example of transmittance of the NIR ray cutoff filter made of synthetic resin as a commodity. Thickness, 0.5 mm; Cu(II) ion content, 8.0 wt %.

ple. The filter has already been mounted on a camera, as well as a commercialized CCD camera.

CONCLUSION

The conclusions obtained in this article are as follows. Cu(II) ion formed six coordinated complexes in acetone with phosphoric acid ester. Cu(II) ion was solubilized owing to intermediate layer formation between Cu(II) and acetone. Cu(II) ion was solubilized through complexation with two PMOE molecules. Cu(II) ion formed chelate structure with two PMOE molecules, and the molecular weight of the complex was low compared with that of the complex formed with DIEHP. The introduction of polymerizable group into ligand made it possible to introduce Cu(II) ion into polymer at a higher concentration. The complex with unpolymerizable ligand caused phase separation in polymer. The solubilized complex formed with phosphate groups was monomeric structure. The plastic filter containing Cu(II) ion through complexation with PMOE showed broad absorption in an NIR range with the peak at around 800 nm. The polymerized filter containing Cu(II) ion complex formed with PMOE had enough NIR cutoff function to actually use.

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