



Polymer-soluble thermostable phosphate-ester copper complexes for near-infrared absorbing dyes with weak absorbance in the visible region

Naoki Hayashi ^{a,*}, Katuichi Machida ^b, Kentaro Otawara ^c, Atsumi Hasegawa ^d,
Nobuyuki Kosaka ^d

^a Process Development Department 1, Process Innovation Research Laboratories, KUREHA CORPORATION, 16 Ochiai, Nishiki-Machi, Iwaki, Fukushima, 974-8686, Japan

^b Process Development Department 2, Process Innovation Research Laboratories, KUREHA CORPORATION, 16 Ochiai, Nishiki-Machi, Iwaki, Fukushima, 974-8686, Japan

^c Process Innovation Research Laboratories, KUREHA CORPORATION, 16 Ochiai, Nishiki-Machi, Iwaki, Fukushima, 974-8686, Japan

^d Analysis & Evaluation Department, Research Center, KUREHA CORPORATION, 16 Ochiai, Nishiki-Machi, Iwaki, Fukushima, 974-8686, Japan

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ABSTRACT

Near-infrared absorbing dyes must be thermally stable above their processing temperatures. Here, polymer-soluble thermostable phosphate-ester copper complexes that meet these requirements are reported for use as near-infrared absorbing dyes with a wide absorption range from 700 to 1200 nm, and a weak absorbance in the visible region. C5–C12 alkyl phosphate-ester copper complexes were synthesized and their thermal stabilities were evaluated by thermogravimetric analysis. The previously reported acetoxy-butyl-phosphate copper complex, which contains an ester group, was also synthesized for comparison. The mass of the alkyl-phosphate-ester copper complexes remained constant up to 170 °C, whereas that of the acetoxy-butyl-phosphate copper complex started to decrease below 100 °C. Some copper complexes showed decomposition temperatures above 250 °C. The thermal-decomposition behavior of the *n*-pentyl-phosphate copper complex, cyclohexyl-phosphate copper complex and 2-ethylhexyl-phosphate copper complex was investigated by thermal-decomposition gas analysis measured by purge-and-trap gas chromatography/mass spectrometry. Cleavage of the O–C bond was the main decomposition reaction for both complexes. The difference in the thermal stabilities of the cyclohexyl-phosphate copper complex and other alkyl-phosphate-ester copper complexes is presumed to result from their different tendencies towards cleavage of the O–C bond. The absorption spectra of the 2-ethylhexyl-phosphate copper complex and the isodecyl-phosphate copper complex showed a broad absorbance from 700 to 1200 nm and a weak absorbance in the visible region. Therefore, these compounds are suitable for window materials that require heat-shielding properties and transparency. The spectra also indicated that the structures of these copper complexes are similar regardless of the substituent on the ligand.

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1. Introduction

Window materials that provide heat shielding from solar energy are essential to improve energy savings and comfort. Direct

circumsolar energy is distributed in the ultraviolet (below 400 nm, 6.9%), visible (400–700 nm, 42.2%), and near-infrared (NIR) (700–2500 nm, 37.7%) regions [1]. In the NIR region, 35.9% of the energy comes from the 700 to 1200 nm range. A reduction of sunlight in this wavelength region can improve heat shielding significantly. A heat-shielding function and a visible-light transparency are important. To meet these requirements, NIR dyes that absorb in the 700–1200 nm region and have a weak absorbance in the visible region are highly desirable for use as window materials [2–5].

* Corresponding author.

E-mail addresses: N-Hayashi@kureha.co.jp (N. Hayashi), katmachida@kureha.co.jp (K. Machida), k-otawara@kureha.co.jp (K. Otawara), atsumi-hasegawa@kureha.co.jp (A. Hasegawa), kosaka@kureha.co.jp (N. Kosaka).

Abbreviations

ABP	acetoxy butyl phosphate
CYP	cyclohexyl phosphate copper
EHP	2-ethylhexyl phosphate
GC/MS	gas chromatography/mass spectrometry
IDP	isodecyl phosphate
IR	infrared
LAP	lauryl phosphate
NIR	near infrared
PEP	n-pentyl phosphate
TGA	thermogravimetric analysis
XXX-C	copper complex, where XXX is the abbreviation of the phosphoric acid ester used as the raw material

Various NIR absorbing compounds have been developed. Fabian reviewed commonly used NIR absorbing dyes [6]. Recently, cyanines [7], azo compounds [8], dithiolenes [9], nickel complexes [10], and boron–bipyromethene [11] have been developed as NIR absorbing dyes. However, most of these NIR absorbing dyes also absorb in the visible region, and the materials are strongly colored. Phthalocyanines [12] and polymethine [13] that have been modified to reduce absorption in the visible region have been reported. However, because the NIR absorption band is narrow, it is difficult to achieve sufficient heat shielding. In general, organic dyes have a low light stability, and therefore they are unsuitable for use in environments that are exposed to sunlight for long periods, e.g., windows. Metal-nanoparticle dispersions have also been developed as NIR absorbing, heat-shielding materials. For example, LaB₆ [14] and cesium-tungsten-oxide nanoparticle dispersions have been developed [15], but they also absorb in the visible region and are strongly colored, like organic dyes. Indium-tin-oxide [16] and antimony-doped-tin-oxide [17] metal nanoparticles show a weak absorbance in the visible region; however the absorption wavelength region is 1300 nm or more.

Copper complexes have been examined as possible NIR absorbing dyes with a weak absorbance in the visible region. The d–d transitions of metal complexes are weak, because they are forbidden transitions, and d–d transitions are rarely used in dyes. However, four- or six-coordinated copper complexes have a single absorption in the 600–800-nm region that results from the ${}^2E_g \rightarrow {}^2T_{2g}$ electronic transition of the single unpaired electron. Moreover, this absorption is broad as a result of the splitting of the orbital energy level by Jahn–Teller distortion. The wavelength of this absorption can be controlled by changing the ligand structure, which affects the ligand-field splitting energy as presented in the spectrochemical series. Quantitative scales that summarize approximately 100 types of ligand are available, and phosphoric acid (PO_4^{3-}) is considered a low wavenumber ligand [18]. Thus, the Cu^{2+} absorption is shifted out of the visible region and into the NIR region by using phosphoric acid, or a related compound, as a ligand. Indeed, Katono et al. have reported a NIR cut-off filter that consists of a copolymer of a (methacryloyloxy)ethyl-phosphate copper complex and methyl methacrylate, in which the copper complex was incorporated as part of the polymer chain through the methacryloyloxy group in the phosphate ester [19,20]. This filter showed desirable spectral characteristics, with absorbances in the 700 to 1200 nm region and a weak absorbance in the visible region. This resin material has a broadband absorption in the 700–1200 nm region and a high visible-light transmission. Although it has a low extinction coefficient, it is highly suitable for use as a heat-shielding

window material.

Processing methods for the resin material are limited because cross-linking occurs through the phosphate ester or copper ion. It is not possible to use a processing method that is suitable for mass production, such as extrusion molding or injection molding. Thus, the use of phosphate-ester copper complexes as a general-purpose material, such as a window material, is limited. To expand the applicability of the phosphate-ester copper complexes, they have also been incorporated in a modified form as NIR absorbing dyes [21], rather than as part of the polymer chain. To use these complexes as NIR absorbing dyes, they must be soluble in the polymer matrix and thermally stable to withstand high processing temperatures. It has been reported that the acetoxy-butyl-phosphate (ABP) copper complex (ABP-C) can form a composite with poly(methyl methacrylate) (PMMA), and this complex has been applied in a thermoplastic NIR cut-off filter [21]. ABP contains an ester group that is similar to the PMMA side-chain structure, which enables the copper complex to dissolve in PMMA. However, the thermal stability of phosphate-ester copper complexes has not been discussed previously. The processing temperatures of typical transparent resins are as follows: ethylene vinyl acetate copolymer 120–230 °C, polyvinyl butyral 150–250 °C, polyvinyl chloride 160–210 °C, polystyrene 170–280 °C, PMMA 190–290 °C, and polycarbonate 270–380 °C. The copper complexes must be thermally stable above the processing temperature. The thermal stability of ABP-C is expected to be low because of the ester group in the ABP substituent; however, it is highly plausible that the thermal stability will be improved by using alkyl substituents on the phosphate ester.

In this study, the copper complexes of the C5–C12 alkyl phosphate esters were synthesized and their thermal stability was investigated. The chemical structures of the C5–C12 alkyl phosphate esters are shown in Fig. 1. Previously reported ABP-C, which contains an ester group, was also synthesized for comparison. The thermal stability was measured by thermogravimetric analysis (TGA) and is discussed in terms of the substituents on the phosphate esters. The thermal-decomposition behavior was investigated by analyzing the pyrolysis products by purge-and-trap gas chromatography/mass spectrometry (GC/MS). First, the major details of the thermal decomposition of the phosphate copper complexes were elucidated, and then the performance of these complexes as NIR absorbing dyes was illustrated by measuring their ultraviolet, visible, and NIR spectra.

2. Experimental

2.1. General

Copper acetate monohydrate (analytical-reagent grade, purity > 99.0%), toluene (analytical-reagent grade, purity > 99.0%), and 1,2-dimethoxyethane (analytical-reagent grade, purity > 99.0%) were from Kanto Chemical Co. n-pentyl phosphate (PEP) was from Alwlsn. 2-ethylhexyl phosphate (EHP) and isodecyl phosphate (IDP) were from Daihachi Chemical Co. Lauryl phosphate (LAP) was from Johoku Chemical Co. All phosphate esters were mixtures of the mono- and di-esters (molar ratio = approx. 1:1).

2.2. Synthesis

2.2.1. General procedure for the synthesis of phosphate-ester copper complexes

The copper complexes were synthesized following a similar procedure to that reported in a patent application [22]. A 200-ml four-necked flask with an attached Dean–Stark apparatus was

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