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Reversible Coloring/Decoloring Reaction of Leuco Dye Controlled by Long-chain Molecule

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Abstract

Leuco dye indicates the reversible coloring reaction with acidic compounds (called developer) having long-chain moiety. In order to clarify the structural change between colored state and decolored one of this system, X-ray diffraction (XRD) measurements and transmission electron microscope (TEM) observations were performed. It was found that mixture of leuco dye and developer took different layered structures between colored and decolored state. This structural change shows intercalation and deintercalation of leuco dye occur in the reversible coloring process. The mechanism of coloring/decoloring reaction of leuco dye with long-chain molecule is proposed.

Keywords: Leuco dye; Reversible coloring reaction; Long-chain molecule; Rewritable paper

1. Introduction

In recent years, a large amount of paper has been used to display digitalized information temporarily. Nowadays, recycling of used papers is very important problem. From view points of waste reduction, various reversible image formation systems have been proposed and developed [1-16]. Leuco dyes have attracted much attention as new imaging media since they have a potential of reversible colored-decolored reaction with acid. Reaction of leuco dye from colorless state to colored one has been applied already in thermal recording system [17]. In this system, phenol derivatives are used widely as acidic compounds (called the developer). It is well-known that lueco dyes indicate reversible coloring/decoloring reaction in liquid phase based on the change of acidity [18]. If hydration and dehydration of leuco dye could control by external stimulus such as heat or pressure in solid phase, rewritable printing system can be fabricated. In 1990s, it has been reported that coloring/decoloring reaction of leuco dye can be controlled by heat using developers with long-chain alkyl groups [1-4]. Recently, practical rewritable printing system using a paper substrate is developed [5-7]. However, detailed reaction mechanism remains unclear.

In this study, structural changes of leuco/developer mixture in solid phase are investigated in order to clarify the coloring/decoloring reaction of leuco dye.

2. Experimental details

6'-(Diethylamino)-3'-methyl-2'-(phenylamino)spiro[isobenzofuran-1(3H),9'-[9H]-xanthene]-3-one (ODB) and *N*-(4-hydroxyphenyl)docosanamide (PA21) were used as leuco dye and developer with long-chain alkyl group, respectively. Melting point of PA21 is 140 °C. Molecular structures of ODB and PA21 show in Fig. 1. The sample films were prepared by following procedure. Mixture of PA21/ODB (6/1; molar ratio [2,4]) sandwiched two substrates was melted on a hot plate kept at 180 °C. Colored film was obtained by rapid cooling with immersion of the molten mixture into ice-bath. Decolored film was obtained by reheating of colored film at kept at 100 °C for 30 seconds and spontaneous cooling in the air.

Ultraviolet-visible (UV-Vis) absorption spectra of the films were recorded using a Shimadzu UV-2200 spectrometer. Samples for UV-Vis measurement were prepared on the cover glasses (thickness 0.12–0.17 mm). Chemical structure of ODB in the films was investigated by Fourier transform infrared (FTIR) spectroscopy using a Shimadzu FTIR-8100 spectrophotometer. Samples for FTIR measurements were prepared on the KBr substrate. The crystal structure of the films was investigated by X-ray diffraction (XRD) measurement and transmission electron microscope (TEM) observation. Fine powder scratched off from cover glasses was prepared as a sample for XRD measurement. Samples for TEM observation were prepared on mica substrate coated carbon film prepared by vacuum deposition. The specimen film was separated with carbon film from the mica substrate and transferred onto a microgrid. The specimen film was exposed ruthenium tetraoxide (RuO_4) aqueous vapor in order to stain [7,19-21]. The XRD apparatus and TEM used here were Rigaku Rint2000 X-ray diffractometer with Cu-Kα radiation source and Hitachi H-7100, respectively.

3. Results and discussion

When PA21/ODB mixture was heated on a hot plate kept at 180 °C, the mixture completely melted and the molten mixture colored dark red. The color of the molten mixture gradually disappeared during slow cooling in the air. When the molten mixture was cooled rapidly with immersion into ice-bath, on the other hand, the mixture remained black. The color of rapidly cooled mixture disappeared by reheating at 100 °C. Colored/decolored reaction was reversible above a hundred cycles.

Figure 2 shows UV-Vis spectra and photographs of colored and decolored PA21/ODB films. Two absorption peaks with almost same intensity appear at 460 nm and 580 nm in the spectrum of colored film. These peaks are the relationship with complementary color each other. Therefore, the colored film is black, as shown in Fig.2 (a'). In contrast, the decolored film has no absorption in the visible wavelength region, resulting colorless and transparent.

Figure 3 shows FTIR spectra of colored (a) and decolored (b) samples. The absorption intensity of the decolored sample at 1760 cm^{-1} is stronger than that of the colored one. There were no absorption peaks in the absorption spectrum of PA21 in the wave number region between 1700 cm^{-1} and 1800 cm^{-1}. Absorption band at 1760 cm^{-1} was assigned to C=O stretching vibration of a lactone ring in the lueco dye [22]. It is concluded that deprotonation from ionized lueco dye with heating occurs even in the solid phase.

Figure 4 shows XRD patterns of PA21 powder and colored and decolored samples. XRD pattern of PA21 powder shows several diffraction peaks in the low angle region (2θ = 2.6°, 4.0°, 5.3°, 8.0° and 10.8°). These are diffraction peaks corresponding to the lattice spacing of approximately 6.6 nm and its higher-order reflections. The molecular length of PA21 calculated from WinMopac V2.0 is 3.4 nm. Therefore, it seems that PA21 molecules stack in the crystal taking head-to-head layered structure such as fatty acid. Three diffraction peaks also appeared at 2θ = 19.7°, 23.5° and 28.6°. These are the reflections from the (110), (200), and (210) planes of PA21 crystal with orthorhombic system, respectively. XRD pattern of the PA21/ODB mixture in colored state shows a very weak and broad diffraction peak around at 2θ = 3.6°–3.9°. This peak is comparable to that at 2θ = 4.0° of PA21crystal. This indicates that layered structure also exists in the colored state of the mixture. On the other hand, XRD pattern of the PA21/ODB mixture in decolored state is quite similar to that of PA21 powder.

In order to clarify fine structural change in colored/decolored reaction, TEM observation was carried out. Figure 5 shows TEM images and high resolution electron diffraction (HRED) patterns of PA21 powder and colored and decolored samples. TEM image of PA21 powder indicates fiber structure and many stripes observe in the fiber. This indicates that PA21 takes layered structure like as fatty acid molecules in the crystal. There are several diffuse diffraction arcs in HRED pattern of PA21 powder. These are the reflections from the (010), (110), (200), (210) and (020) planes of PA21 crystal, respectively. HRED pattern is good agreement with XRD pattern in the scattering angle form 15° to 30°. TEM image of colored sample also indicates layered structure. Careful observation finds that layer spacing of layered structure in colored state is slightly longer than that of PA21 powder. HRED pattern of colored sample shows halo and diffuse diffraction arc with interplanar spacing of about 0.4 nm^{-1} which is comparable to broad diffraction peak around at $2\theta = 20°–24°$ in XRD pattern (Fig. 4 (b)). Consequently, it is concluded that PA21 molecules crystallize taking a lamellar structure with ODB in the mixture of colored state and this lamellar structure is disorder. In decolored state, layered structures cut into small pieces. HRED pattern of decolored sample shows similar pattern obtained from PA21 powder although diffraction intensities of each reflection are weak. PA21 molecules in decolored state seem to crystallize taking same crystal structure of PA21 powder.

Figure 6 represents the structure change of the PA21/ODB mixture during coloring/decoloring reaction. PA21/ODB mixture melts by heating and changes into the molten mixture. When the molten mixture is cooled rapidly, ODB molecules are intercalated into the layered structure of PA21 and lamellar structure described as PA21/ODB/PA21 is formed with PA21 and ODB. When the colored mixture is reheated at 100 °C which is lower than the melting temperature of PA21, molecular motion of long alkyl chain of PA21 becomes actively and tends to crystallize by themselves. Self-crystallization with PA21 molecules gives rise to release ODB molecules intercalated between lamellae, resulting color disappearance. Consequently, it is concluded that reversible coloring reaction of PA21/ODB mixture is caused by intercalation and deintercalation of ODB with structure change of PA21 crystal.

4. Conclusions

The mixture of PA21/ODB showed a reversible coloring/decoloring reaction controlled by heat-treatment in solid phase. XRD and TEM observations revealed that PA21 molecules stacked taking head-to-head layered structure. Colored mixture was composed of lamellar structure formed by intercalation of ODB into the PA21 layers. When the colored mixture was reheated at 100 °C, PA21 molecules crystallized by themselves and the color disappeared by release of intercalated ODB. The structure change of PA21 crystal induced a reversible coloring reaction of the PA21/ODB mixture.

Acknowledgement

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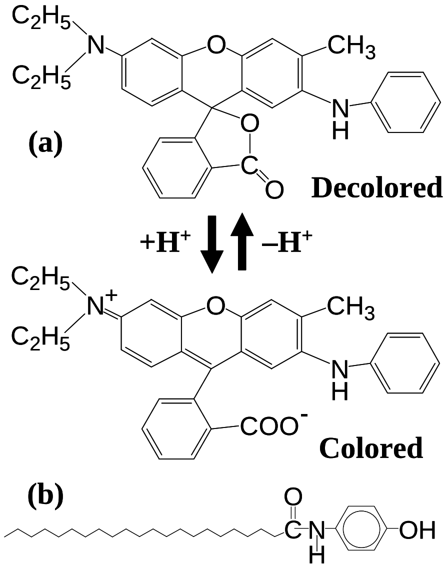

Fig. 1. Coloring reaction of ODB (a) and molecular structure of PA21 (b).

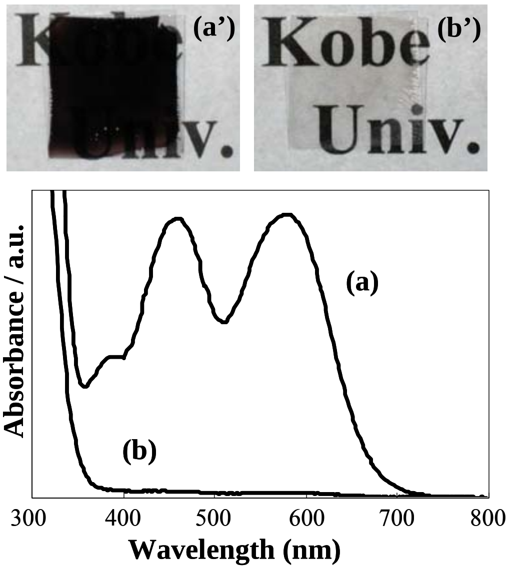

Fig. 2. UV-Vis. absorption spectra and photographs; colored (a, a') and decolored (b, b') samples of PA21/ODB mixture.

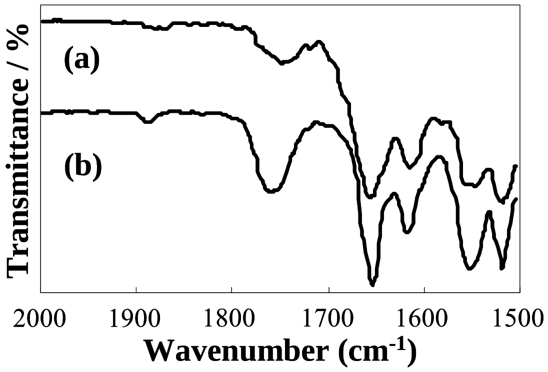

Fig. 3. FTIR spectra of colored (a) and decolored (b) samples of PA21/ODB mixture.

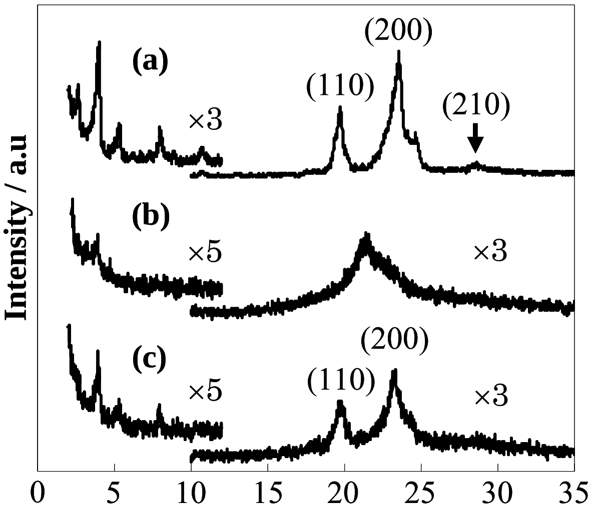

Fig. 4. XRD patterns of PA21 powder (a), colored (b) and decolored (c) samples of PA21/ODB mixture.

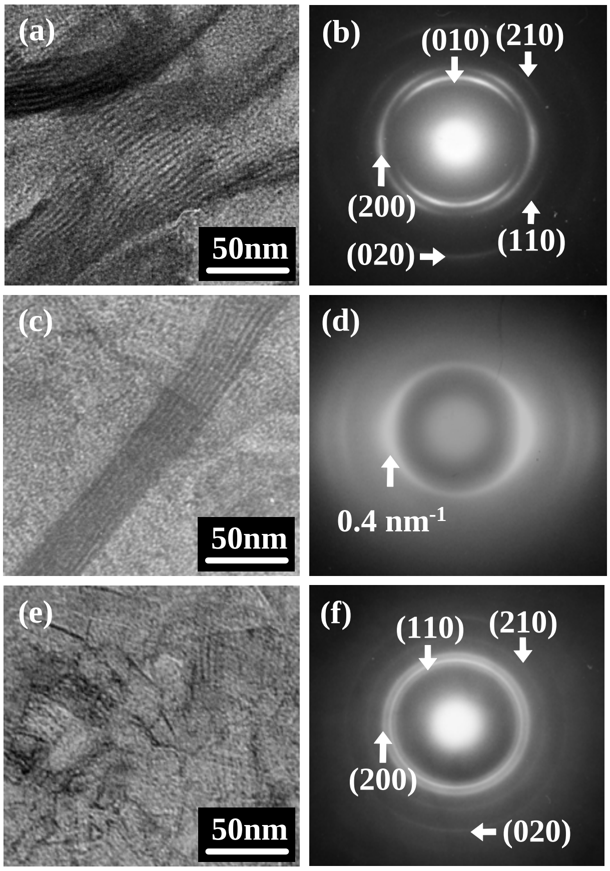

Fig. 5. TEM images of PA21 powder (a b), colored (c d) and decolored (e f) samples of PA21/ODB mixture

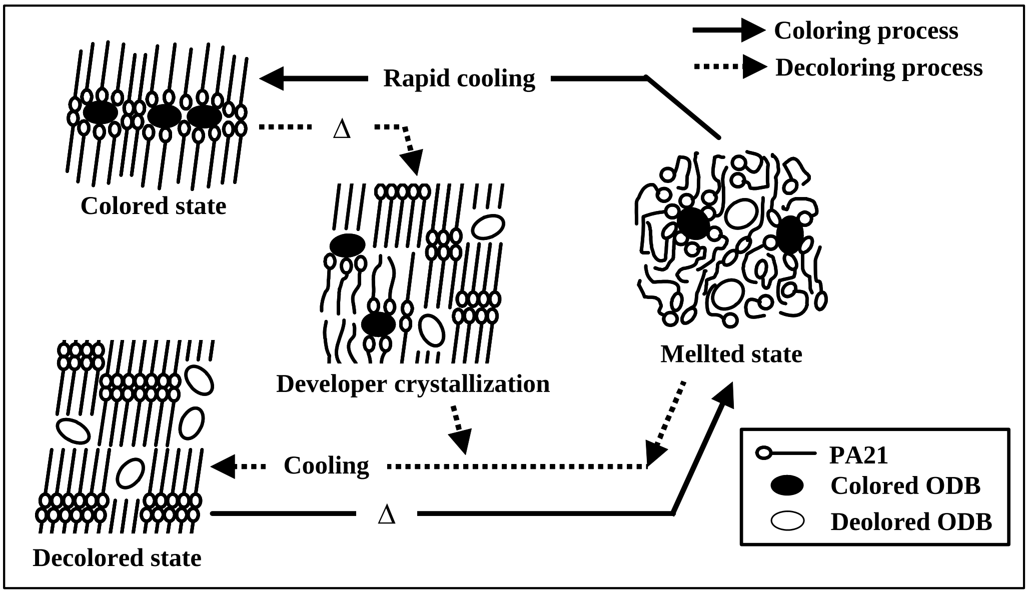

Fig. 6. Mechanism of reversible coloring/decoloring reaction of PA21/ODB mixture.