Molecular Design for Coloring/Decoloring Properties in Rewritable Paper Using Leuco Dyes: Effects of Long-chain Alkyl Group

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Abstract
Printing systems with an information-display function are attracting increasing interest as greater volumes of information become available in digital format. We recently developed a practical rewritable printing system for displaying documents in which the coloring-decoloring reaction cycles are thermally controlled using leuco dyes. This system is composed of leuco dye molecules and acidic developer molecules with long-chain alkyl groups and associative groups; it exhibits colored/decolored states that can be reversed by varying the heat conditions. Since the reversibility property mainly depends on the molecular structure of the developer, we prepared simple developers with different alkyl lengths to investigate the structural effects. We found that controlling the physical properties of the long-chain alkyl group of the developer is the key to achieving both thermal stability of the colored state and rapid erasability.

Introduction
It was initially thought that the digitization of information would dramatically reduce the volumes of paper used in the office, but in reality the volume has continued to escalate. We thus developed a practical rewritable printing media using a paper substrate that can be printed on more than 500 times. This "rewritable paper" reduces the consumption of paper for temporary use.

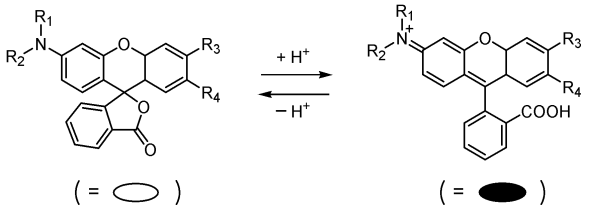

Figure 1. Leuco dye reversible color reaction

A practical rewritable printing system must at least satisfy three requirements: (1) high-contrast images, (2) thermal stability of the displayed images, and (3) fast and easy erasing and rewriting. We thus investigated the use of leuco dyes, which change from a colorless state to a colored one through a reaction with an acidic compound (called the developer). The reaction is reversible, as one can see from Figure 1. We focused our efforts on ways to control this reversibility by using heat. We designed a developer with a long-chain alkyl group and intermolecular association groups to induce phase separation from leuco dye through developer crystallization.

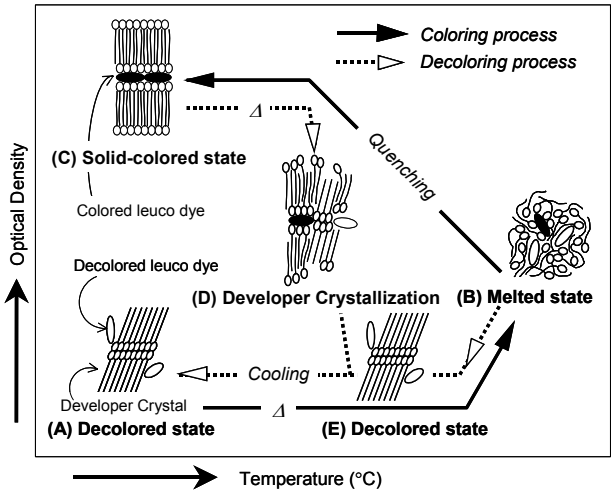

Figure 2. Coloring/decoloring mechanism of leuco dye/long-chain developer systems

The coloring and decoloring processes of a mixture of long-chain developer and leuco dye are illustrated in Figure 2. Applying heat to the mixture when it is in the decolored state (A) converts it to a melted state (B); quenching the melted-state mixture switches it to a solid-colored state (C). Then, reheating the colored mixture (C) to a temperature less than the melting temperature returns the developer to a stable crystalline state and the color disappears (D-E). After cooling, the state returns to the decolored state (A). If the mixture in the melted state (B) is allowed to cool down slowly, the color gradually disappears.

Results and Discussion
Molecular Design for Developer
The coloring/decoloring process is mostly determined by the molecular shape and structural transformation of the developer. A well-known developer is PU18, a long chain of phenol-urea molecules with 18 carbon atoms. PU18 contains phenol, urea, and octadecyl groups and exhibits excellent coloring/decoloring properties. On the assumption that a long-chain alkyl group introduced into the developer provides reversibility in almost all cases, it is necessary to accurately understand how an alkyl chain

attached to the developer works during the coloring/decoloring process, in order to acquire the guidelines for molecular design for practical application. We therefore examined different types of phenol-urea developers with various numbers of carbon atoms (n_c = 15–22), as shown in Figure 3. We synthesized them using condensation reactions between alkyl isocyanate and *para*-amino phenol.

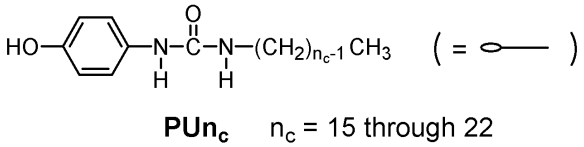

Figure 3. Phenol-urea developers (PUn_c) with different numbers of carbon atoms (n_c)

Thermal Properties of Colored State

We carried out differential scanning calorimetry (DSC) (5°C/min) and optical density measurements (3°C/min) while heating the mixture after quenching. A mixture of leuco dye and developer sandwiched between two glass slides was melted at 160°C and quenched at 0°C. Figure 4 shows the DSC heating thermopeaks of eight phenol-urea developers (PUn_c), each of which exhibited two exothermic peaks and one endothermic peak. For example, the PU with n_c = 22 showed a large exothermic peak at 62°C, a small exothermic peak at 105°C, and a large endothermic peak at 140°C.

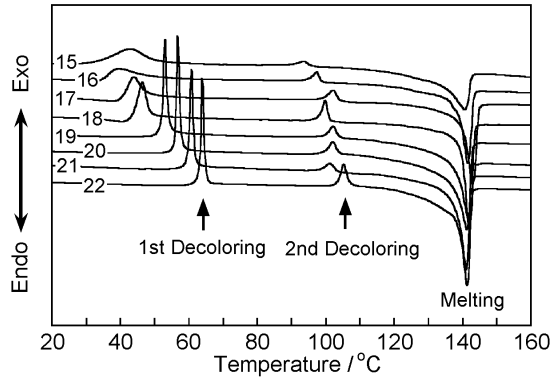

Figure 4. DSC heating thermograms of leuco/PUn_c mixtures (5°C/min)

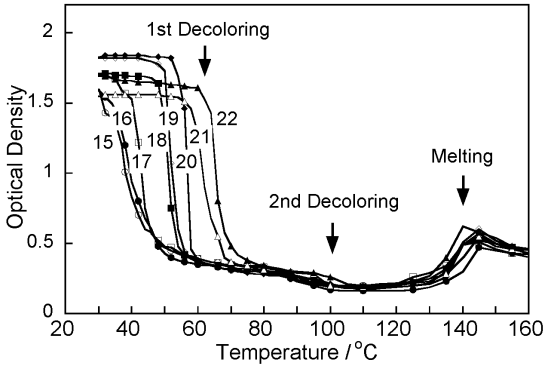

Figure 5. Decoloring temperature characteristics of rewritable media using PUn_c on heating at 3°C/min

As shown in Figure 5, extensive decoloring occurred at the temperatures where the large exothermic peaks were observed, and there was a slight change in the optical density at the temperatures where the small exothermic peaks were observed. We refer to the former as the "first decoloring point" and to the latter as the "second decoloring point". These points shifted to the right as n_c was increased, and the peaks of the former were larger than those of the latter. Melting at around 140°C caused the endothermic peak beyond the second decoloring point. Correspondingly, the optical density gradually increased until 140°C, meaning that the leuco dye/PU mixture melted at this temperature. Coupling of the leuco dye with the developer increased the optical density.

Dynamic Transition from Colored to Decolored State

Figure 6 shows *in situ* synchrotron radiation X-ray diffraction (SR-XRD) patterns of the PU18 taken during the conversion from the colored to decolored states observed using the DSC and optical density measurements. The SR-XRD measurements were done on beam lines 9C and 15A at the Photon Factory (PF), a synchrotron radiation facility in the National Laboratory for High-Energy Physics (KEK), Tsukuba, Japan. The PF operates at 2.5 GeV; the X-ray wavelength (λ) is 0.15 nm. Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) spectra were recorded simultaneously every 10 s with two gas-flown one-dimensional, position-sensitive detectors.

At 20°C, there was a SAXS peak of 42.0 Å corresponding to the lamella distance and a WAXS peak of 4.0 Å corresponding to the lateral packing. This means that the colored state of the leuco/PU18 mixture was in a smectic-type liquid crystalline phase. As the temperature was increased from 20 to 110°C, dramatic changes in the SAXS and WAXS patterns occurred at the two temperatures corresponding to the first and second decoloring points (see Figures 4 and 5).

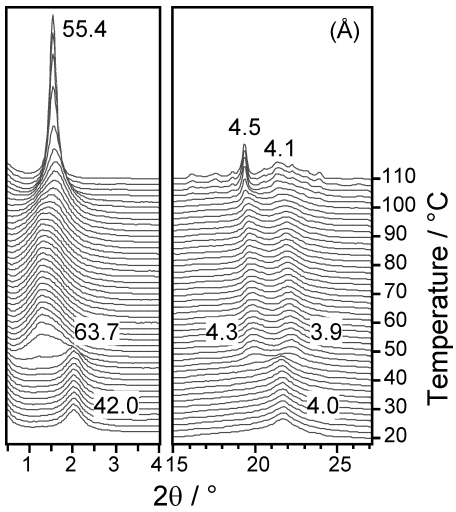

Figure 6. XRD spectrum changes during decoloring of leuco dye/long-chain developer PU18 mixtures (synchrotron radiation X-ray diffraction; temperature increase at 2ºC/min)

At the first decoloring point, the SAXS peak increased to 63.7 Å, and the WAXS peak was split into two peaks of 3.9 and 4.3 Å. These patterns remained unchanged until 100°C, where they again changed dramatically. The broad SAXS peaks shifted from 63.7 to 55.4 Å with increased intensity and became very sharp at 110°C. The two broad WAXS peaks likewise became very sharp at 110°C. These changes mean that the crystallinity of the leuco/PU mixture was dramatically increased at the second decoloring point. The same pattern was observed for the long-chain alkyl developers of PU21 and PU22.

Figure 7 summarizes the relationships between the first and second decoloring points and the melting points of the leuco dye/PUn_c mixture and of pure PUn_c with n_c = 15–22. The increase in the first and second decoloring points as n_c increased indicates that the thermal stability of the colored state can be improved by simply increasing the length of the alkyl chains connected to the urea group. Interestingly, the rate of increase of the first decoloring point with n_c was higher than that of the second. That the melting points of the leuco dye/PUn_c mixture and of pure PUn_c remained virtually unchanged as n_c was changed indicates that the leuco dye/PU crystal structure was mainly stabilized by intermolecular hydrogen bonding of the urea-urea and phenol-phenol groups of the developer and that this restricted structure dominated the total cohesive energy.

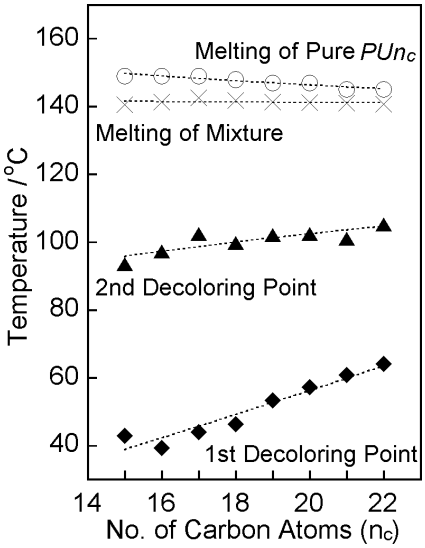

Figure 7. Relationships of thermopeaks between coloring/decoloring states

From these results, we propose a mechanism for the morphological changes in PU18 as it transitions from the colored to the decolored state. In the colored state, it has an interdigitated structure (Figure 8a), in which the alkyl chains are packed close side by side between the spaces formed by the combined structure of the leuco dye and phenol group, promoting intermolecular alkyl interactions. This structure is reasonable if we consider the molecular length of PU18 to be 32.0 Å, as calculated by MM2, and that of leuco dye to be about 10 Å, giving a lamella distance of 42.0 Å. This accounts for the increase in the first decoloring point with increasing n_c by alkyl van der Waals forces. We assume that the long chains of the developer are arranged normal to the decoloring plane in the slightly colored state above the first decoloring point (Figure 8b), where the leuco dye/PU complex was dissolved. The structure shown in Figure 8b is still metastable, and disordering in the molecular packing is not excluded, as revealed in the broad SAXS and WAXS patterns (Figure 6). Therefore, a certain amount of the leuco dye/PU complex is present. As the temperature increases, this metastable structure transforms into a stable crystalline phase (Figure 8c) in which the alkyl chain is inclined against the lamella plane, reducing the lamella distance from 63.7 Å (Figure 8b) to 55.4 Å (Figure 8c). In this phase, the crystal packing is the densest, preventing any complexation with the leuco dye molecules and resulting in the lowest optical density.

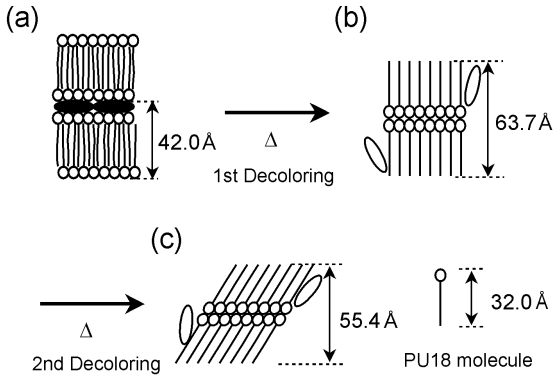

Figure 8. Illustration of postulated morphological changes from colored to decolored state

In short, thermal stabilization of the colored state can be achieved by increasing the n_c of the developer, whereas the melting point of the developer is not affected by its chain length for materials design of rewritable paper.

Coloring/Decoloring Performance of Rewritable Paper

We prepared rewritable paper samples using the leuco dye/PUn_c mixture and used them to study rapid erasing. Figure 9 shows the structure of the paper. It changed color when heated to over 145°C, enabling printing of high-contrast black images. Color can then, in almost all cases, be mostly erased over the second decoloring point by using an eraser heater with a heating time of several tens of milliseconds.

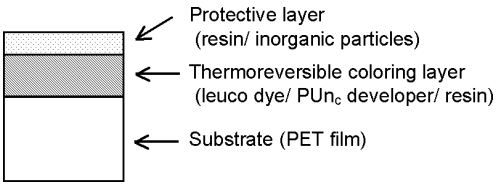

Figure 9. Basic structure of rewritable paper

When a thermal head with a several-millisecond heating time was used as the heat source, the samples had different degrees of erasability. The medium with n_c = 14 showed about 50% erasability, but the one with the longest n_c (22) showed the best

result (90% erasability) (Figure 10). We found that the erasing speed is closely related to the crystallization rate of pure developer and that the crystallinity can be improved by increasing n_c. These results show that alkyl chain as increased n_c makes crystallization and separation from leuco dye easy and promotes conversion to a stable decolored state even with a short heating time. Erasability can be speeded up by increasing n_c.

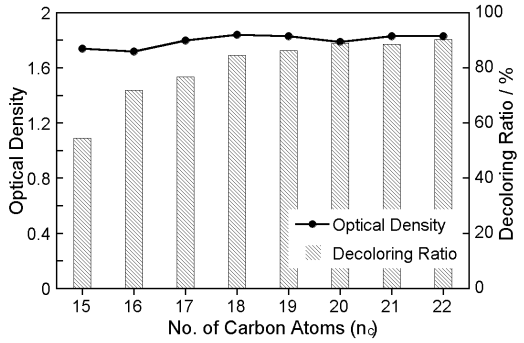

Figure 10. Erasing characteristics of rewritable papers using PUn_c

Conclusion

We synthesized phenol-urea developers with different numbers of carbon atoms and investigated the effects of the developer alkyl chain lengths on reversibility. The length of the chains greatly affected the thermal stability and erasability. Rewritable paper has already found a number of practical applications in Japan, including the information display portions of magnetic cards and IC cards. When people want to use digital information for various purposes, they often automatically print it out. Rewritable paper is a very effective way to print out information that is needed only temporarily.

Acknowledgement

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Author Biography

Satoshi Yamamoto joined Ricoh Japan in 2003 after receiving on M.S. degree in applied chemistry from the Graduate School of Engineering, Kyushu University, Japan. His current interest is investigating materials for reversible recording.