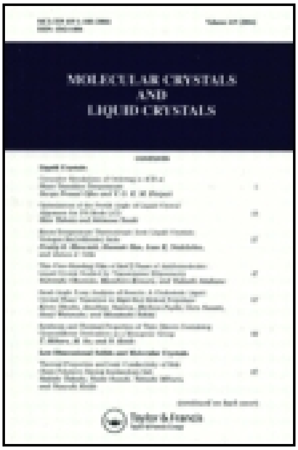

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Thermal Degradation of Organic Dye for Recordable Optical Media

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Thermal Degradation of Organic Dye for Recordable Optical Media

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The degradation of a dye on a compact disc-recordable (CD-R) during recording was analyzed quantitatively using a spectroscopy and a thermal gravimetric analysis. It was found that the degradation resulting in the decrease of absorbance was completely different from that accompanied by weight loss. The calculated temperature and the rate constants showed that the type of degradation with the decrease in absorbance due to partial bond cleavages of the dye molecules, not with weight loss, was a major one producing optical signals in the dye layer.

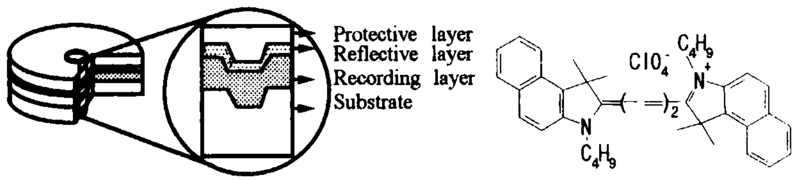
Keywords : optical media; write once; thermal degradation; cyanine dye; CD-R

INTRODUCTION

Recently, recordable (Write Once Read Many : WORM) optical media such as compact disc-recordable (CD-R, 780ñm) and digital versatile disc-recordable (DVD-R, 650nm) using organic dyes attract considerable attention because of their compatibility with conventional CD and DVD systems and strong demand for economical high capacity storage. The media have a simple structure of 4 layers consisting of a polycarbonate (PC) substrate, a dye recording layer fabricated by spin-coating, a reflective layer and a protective layer as shown at figure 1, and therefore they are relatively cheap compared with other metal-based optical media.

Up to now, the recording mechanisms of CD-R have been explained by the thermal deformation of each layer resulted from the thermal degradation of the dye and the recording characteristics were thought to be closely related with the degree of deformation of each layer[1-4]. However, most of researches on the thermal degradation have been focussed on the weight loss. And this has been considered as a main mechanism in the optical recording.

In this paper, the thermal degradation of a dye on a CD-R was investigated by observing the change of the absorption spectra and the weight loss by a thermal gravimetric analysis (TGA) to find the sources of optical signals after recording.



(A) (B)

FIGURE 1 Descriptive structure of a CD-R (A) and the chemical structure of the dye used in the experiment (B).

EXPERIMENTAL

Preparation and Recording of the CD-R

A CD-R disc was prepared using a conventional CD-R fabrication procedure, spin coating of a dye solution (conc. = 5.0%) on a pregrooved PC substrate (groove depth=130nm, groove width = 400nm by AFM (PSI, AutoProbe)), sputtering of a gold reflective layer on the dye layer and spin coating of a UV-curable resin to form a hard protective layer. The dye used is one of the typical CD-R dyes (NK-3219, 2-[5-(1,3-Dihydro-1,1 -dimethyl-3-butyl-2H-benzindol-2-ylidene)-1,3-pentadienyl]-1,1-dimethyl-3-butyl -1H benzindolium perchlorate, from Japanese Research Institute for Photo-sensitizing Dyes Co., Ltd.) and its chemical structure is shown at figure 1.

To observe the thermal degradation of the dye during optical recording, the CD-R is recorded by a CD-R evaluation system equipped with a 780nm laser diode(Apex Systems, OHMT 500), where recording power is 10mW at 1.3m/sec (1x speed recording). The surface area focussed by the recording beam on groove and land are approximately 50% and 20%, respectively. And the volume of the dye on groove occupies about 44% in total based on the analysis of scanning electron microscopy (SEM).

Absorption Spectra Analysis

To observe the thermal degradation of the dye layer, the dye was coated on a slide glass and heat-treated in a hot stage (Mettler FP82HT) with changing temperature. The changes of absorption spectra after washing the dye films treated at different temperatures were observed by UV spectrophotometer (Varian, Caryl 3E).

Weight Loss Analysis

The weight loss of the dye above the thermal degradation temperature was measured with varying temperature by TGA (Polymer Laboratories) to correlate the weight loss behaviors with those of the spectra.

RESULTS AND DISCUSSION

Approximately 17% of decrease in absorbance was observed at the maximum absorption wavelength considering the dye concentrations in a solvent before and after recording, which means the degree of decomposed dye during the recording. The volume of the dye layer focussed by the recording beam will be about 33% ($44\% \times 0.5 + 56\% \times 0.2$). Therefore, the amount of decomposed dye in the focussed dye layer by the laser recording is about 50%.

The rate of degradation was measured by two different methods. One is to detect the change of the absorbance induced by the dye degradation, and the other is to measure the weight loss directly by TGA. As is shown at figure 2, even though the weight at 270℃ in the TGA thermogram kept 50% of the initial value, the change of absorption obtained from the glass treated with the same temperature in the hot stage showed that the degradation has already completed. As can be seen at figure 3, there is big difference in the rate constant obtained from the two methods. Assuming that the degradation is a first-order reaction, the rate constants calculated from the decrease of absorbance(k) and the weight loss(k') showed 0.016(sec^{-1}) and 0.0041(sec^{-1}) at 260℃, respectively. These results mean that the degradation inducing weight loss is different from the degradation resulting in the decrease of absorbance. It is thought that the decrease of absorbance is produced by partial bond cleavages and that the weight loss is induced by more crucial bond cleavages.

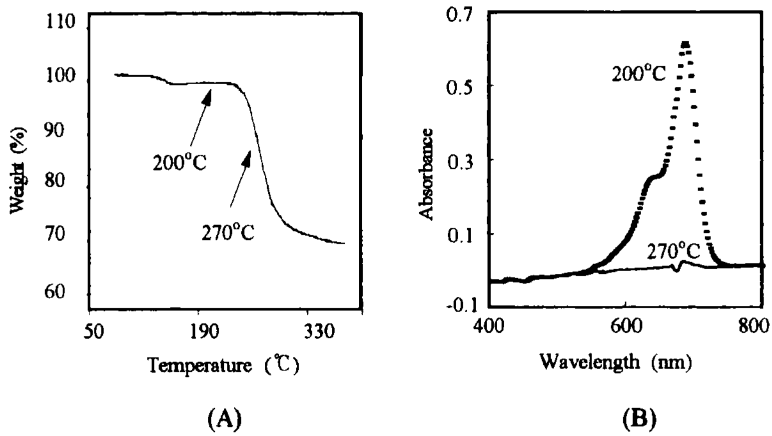


FIGURE 2 The weight loss measured by TGA (A) and the change of absorption after washing the degraded dye (B).

If it is assumed that the degradation with weight loss is also a first-order reaction proceeding within 500nsec[4], the rate constant should be higher than 1.4×10^{6}(sec^{-1}) to reach 50% of degradation ($\ln([R]_t/[R]_o)=-kt$, $k=\ln2/t_{1/2}$). The temperature required to obtain such a high rate constant can be estimated by assumming that the degradation of the dye is an Arrhenius -activated chemical reaction where the temperature dependence of the rate constant can be expressed by

$$k = A\exp(-E_a/RT) \quad (1)$$

, where E_a is the activation energy of the dominant process. The rate constants by the weight loss in TGA at 260, 280, and 300℃ were found to be 4.1×10^{-3}, 1.0×10^{-2} and 1.5×10^{-2}(sec^{-1}), respectively (Fig. 3). According to the Arrhenius equation and the measured rate constants, the temperature required to get 50% of degradation based on only the weight loss-type was found to be over 1000℃, which is much higher than that of the calculated time-dependent thermal profile[4]. That means optical signals from the recorded dye layer in the CD-R is mainly resulted from the degradation with the decrease in absorbance instead of weight loss-type one.

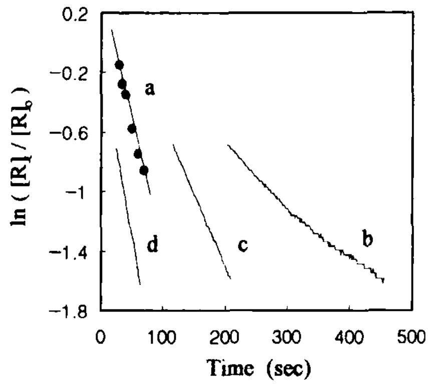


FIGURE 3 Determination of the rate constants of the first order reaction from the change of absorbance(k), and from the weight loss(k'): a, k=0.016(sec^{-1}) at 260℃; b, k'=0.0041 at 260℃; c, k'=0.01 at 280℃; d, k'=0.015 at 300℃.

CONCLUSION

The degradation rate constant of a dye during laser recording was estimated experimentally by a spectroscopy and a thermal gravimetric method.

It was found that the rate of degradation with the decrease in absorbance was much more rapid than that with weight loss, which may be a direct evidence of suggesting another mechanism to understand the recording mechanism of CD-R. The decrease of absorbance may be due to partial bond cleavages resulting in the changes of the optical properties of the dye, on the other hand, the weight loss is induced by more crucial bond cleavages. Accordingly, the degradation of the dye in the CD-R should be considered as a combining process consisting of the partial bond cleavages and of more crucial bond cleavages giving weight loss.

In addition, from an Arrhenius equation and the measured rate constants of weight loss, the temperature required to get 50% of degradation within 500nsec was found to be over 1000℃, which could not be properly explained by the calculated time-dependent thermal profile. As a result, the degradation giving the decrease in absorbance is supposed to be a major one contributing to the changes in the optical properties such as refractive index which is really used in the laser recording.

REFERENCES

1. E. Hamada, Y. Shin and T. Ishigaro, *SPIE Proc.*, **1078**, 80 (1989).
2. A.H.M. Holtslag, E.F. Mecord and G.H. Werumeus Buning, *Jpn. J. Appl. Phys*, **31**, 484(1992)
3. Y.J. Huh, T.Y. Nam, K.Y. Park and S.C. Kim, *Int. Symp. Optical Memories '95*, Technical Digest, P-34, 7 (1995)
4. Y.J. Huh, J.S. Kim, T.Y. Nam and S.C. Kim, *Jpn. J. Appl. Phys*, **36**, 403(1997)