Prefluorescent-Dye-Induced Fluorescent Imaging Based on Polymeric Photobase Generators

Kyu Ho Chae*, Won San Choi, and Yoo Ho Kim

Department of Applied Chemistry, Chonnam National University, Kwangju, 500-757 Korea
*khochae@chonnam.ac.kr

Introduction

In recent years, the formation of fluorescent images in thin polymer films has attracted considerable interest due to their possible application in the areas of optical data storage and displays. Fluorescence imaging has been used with fluorescence probes to study photoacid generation efficiencies and acid diffusion in microlithography, and for mapping photogenerated radicals in thin polymer film.

A number of methods for the formation of fluorescent images have been reported. Most of these methods are based on photogenerated acids. Similar to fluorescent-image formation based on photogenerated acids, fluorescent imaging based on photogenerated base is also possible.

In previous studies, we have reported that the photolysis of oxime-urethane derivatives or a polymeric photobase generator containing oxime-urethane groups led to the formation of amines. In this proceeding, we report on the new approach to fluorescent imaging based on a polymeric photobase generator containing oxime-urethane groups and that containing phthalimide carbamate groups through the use of fluorescamine, a prefluorescent dye for amino group.

Experimental

Polymerization. MMA and a monomer containing oxime-urethane or phthalimide carbamate group were dissolved in THF with AIBN as an initiator. The polymerization was carried out at 60 °C for 20 h. The polymer was obtained by double precipitation in methanol.

Fluorescent patterning. A copolymer film on a slicon wafer was covered with a mask containing a micropattern, and it was irradiated with 254 nm UV light. A latent image was formed on the copolymer film. The latent image was developed with fluorescamine solution.

Results and discussion

Fluorescent Imaging Based on Polymeric Photobase Generator Containing Oxime-Urethane Groups. Scheme 1 shows the chemical reactions which occur during the formation of fluorescent image. Irradiation of copolymer containing oxime-urethane groups led to the formation of pendant amino groups in the irradiated area. Treatment of the irradiated film with fluorescamine resulted in the formation of a fluorescent image.

Scheme 1.

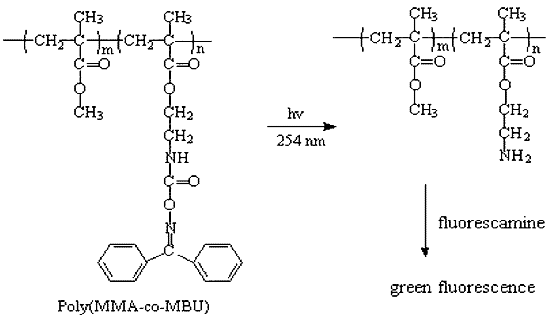

Fig. 1 shows a fluorescent image obtained with a copolymer film. A clear and green fluorescent image with a line width of 2 μm was obtained. The image was stable for more than one year without any loss of original fluorescence intensity.

The fluorescence intensity of the fluorescamine-treated copolymer film or solution was enhanced by the addition of HCl and decreased by the addition of triethylamine. This base-acid reversibility process was complete in the copolymer solution, but was incomplete in the copolymer film.

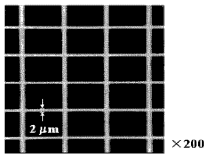

Figure 1. A fluorescent image obtained with a copolymer film containing oxime-urethane groups.

Bi-color Fluorescence Imaging Based on Polymeric Photobase Generator Containing Phthalimido Carbamate Groups.

A copolymer containing phthalimide carbamate groups was applied to a bi-color fluorescent imaging material. Scheme 2 shows a synthetic route for the preparation of copolymers containing phthalimide carbamate groups.

Scheme 2.

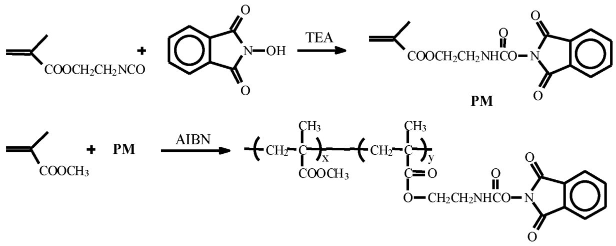

Fig. 2 shows aschematic diagram for the formation of bi-color fluorescent imaging process. A thin copolymer film on a silicon wafer was covered with a photomask and irradiated by UV light. A latent image was formed in the irradiated area. Treatment of this latent image with fluorescamine and rhodamine consecutively, led to the formation of a fluorescent ce image.

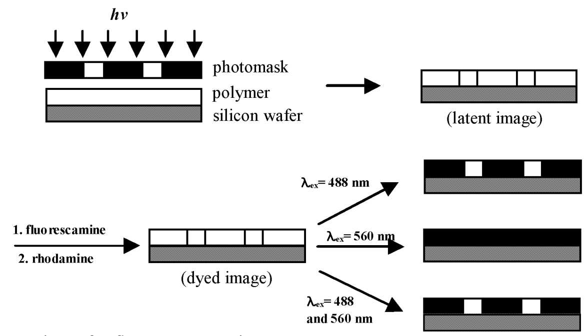

Figure 2. A schematic diagram for the formation of bi-color fluorescent patterning process.

Fig. 3 shows an example of a bi-color fluorescent pattern obtained with a copolymer film on a silicon wafer. Depending on the excitation wavelength, different-colored, fluorescent micropatterns were observed by using a conforcal microscope.

Figure 3. Bi-color fluorescent images observed by a conforcal microscope.

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