Highly Fluorescent Anthracene Polymers for Direct Photo Patterning

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Abstract

Highly fluorescent anthracene polymers, linked by a alkylene unit, were examined for fluorescent patterning. The anthracene polymers were soluble in organic solvent such as chloroform, which allowed solution processing to afford fluorescent thin films using the spin coating method. The fluorescence intensity of the polymer solution as well as film was decreased upon exposure to a high energy UV source, due to the photodimerization of anthracene unit. Utilizing such fluorescence decay, a fluorescent polymer pattern was directly developed from the thin film using a photomask. The photo-patterning of the fluorescent anthracene polymer film afforded a convenient method of image formation and patterning of gap electrode.

Keywords: Photochromic, electrochemical polymerization, photocell, photovoltaic, photocurrent generation,**.**

Introduction

Fluorescent anthracene has been studied for a promising building block or substittuent to obtain π-electron-rich organic polymers[1-2] for the application potential in organic semiconductors, organic transistor and emitting electroluminescent devices.[3-4] Besides, anthracene has been widely used as a signalling subunit for both cation and anion sensing, due to the commercial availability and the high fluorescence (quantum yield in acetonitrile is 0.36).[5] However, only few studies concerning direct photo patterning studies, possibly due to the intractability of the aromatic polymers. It is thus challenging to prepare processible polymers containing anthracene unit for fluorescent thin film patterning process.

We report here the facile formation of patterns on the anthracene polymer films, in which anthracene is dimerized under UV exposure.

Experimental Section

Instruments. The average molecular weight of the polymer was characterized by a gel permeation chromatography (GPC) (model: Waters R-401 ALC/GPC) with THF as an eluent and polystyrene standard for calibration. Fluorescence was measured with luminescence spectrometer (PerkinElmer, Model LS55). The thickness of the film was determined via an Alpha step profilometer (Tencor Instruments, Alpha-step IQ) with an accuracy of 1 nm. The polymer films were illuminated with a high-intensity UV lamp (Spectroline, USA, 40 mW/cm^2), model ENF–260/FE for the pattern experiments through a photomask. The pattern in the anthracene polymer film was examined by a digital camera (Model: Canon Power Shot A640) under UV exposure (10 mW) and a confocal microscope (Carl Zeiss, Inc (LSM 510 META) under the excitation at 405 nm

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Result and Discussion

The weight average molecular weights (M_w) of the anthracene polymers by GPC were 2900 ~ 4950 with M_w/M_n of 2~ 3, depending on the reaction time and monomer composition. The anthracene polymers were soluble in common organic solvents such as tetrahydrofuran, dichloromethane, chloroform and chlorobenzene. The solubility of the anthracene polymers was higher than that of anthracene, possibly due to the attachment of an alkylene spacer as a bridge between the anthracene rings.

UV Patterning of the fluorescent anthracene polymer film

Anthracene undergoes photodimerization under UV exposure,[6-7] to convert non-fluorescent dimmer. Such photoreaction provides a solvent-free dry method of image formation and creation of patterns. By taking advantage of the solubility of the anthracene polymers in organic solvent, thin films of the anthracene polymers could be prepared by a solution process using a spin-coater. Thin films having thickness of 50 nm to 1500 nm could be obtained, depending on the concentration of the polymer and spinning speed. The film coated on a quartz plate showed fluorescence with an emission maximum at ~540 nm. After 30 min. of irradiation with a UV lamp ($\lambda \geq 365$ nm), the emission intensity from the film was significantly reduced and the FT-IR spectrum for the UV exposed film showed that the intensity for C=C (aromatic ring) vibrations at 1631 cm^{-1} and 1557 cm^{-1} were decreased as reported before. The decrease in the intensity of the aromatic C=C vibration could be attributed to the loss of aromaticity in the benzene ring of the anthracene unit which is involved in the cycloaddition, by the formation of dianthracene unit. In addition, UV spectrum of the UV exposed film showed a decrease in the optical density in the absorption region of anthracene and an increase in the absorption region of dianthracene. These results indicative of the photodimerizaiton of the anthracene units in the polymer by the UV exposure.[6, 19]

Such a photodimerization of anthracene unit in the polymeric film led to pattern formation on the anthracene polymer films by UV exposure. Thus, a polymer film (cast from 1-wt.-% chloroform solution) was illuminated with a UV source (intensity of 40 mW/cm^2) through a 0.1-mm-thick gap electrode mask. In this way, uniformly periodic patterns were formed on the anthracene polymers film in a large area. Figure 1 shows the patterned optical image obtained from photo masked irradiation of the polymer film for 30 min. It consists of bright (UV shaded) and dark area (UV exposed for 30min.). Figure 2 shows the patterned fluorescent image of the same film in Figure 1. It consists of fluorescent (UV shaded) and dark area (UV exposed area.).

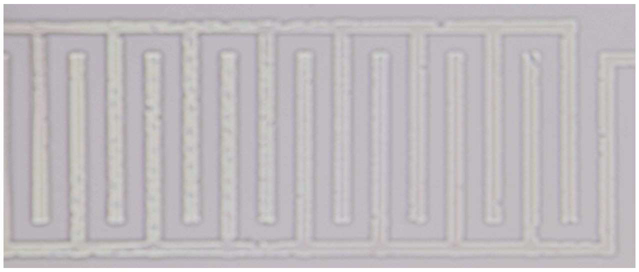

Figure 1. A photograph of the patterned optical image obtained from photo masked irradiation of the polymer film..

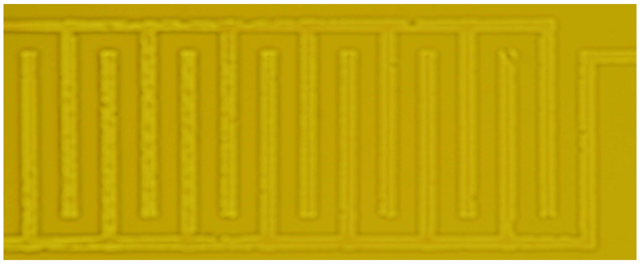

Figure 2. A photograph of the patterned fluorescent image obtained from photo masked irradiation of the polymer film.in Figure 1.

Various fluorescent images with different pattern sizes on the polymer film were formed with a different photomask and radiation dose. Figure 3 shows 1 um pattern formed from the UV process. Such a pattern formation by the soluble anthracene polymers could be extended for the preparation of various fabrications and fluorescent imaging as a dry patterning process.

In conclusion, polymeric anthracene could be patterned with a UV light, resulting in fluorescent patterns. Further synthesis and photo patterning of anthracene polymer films for different image formations plus imaging conditions will be discussed.

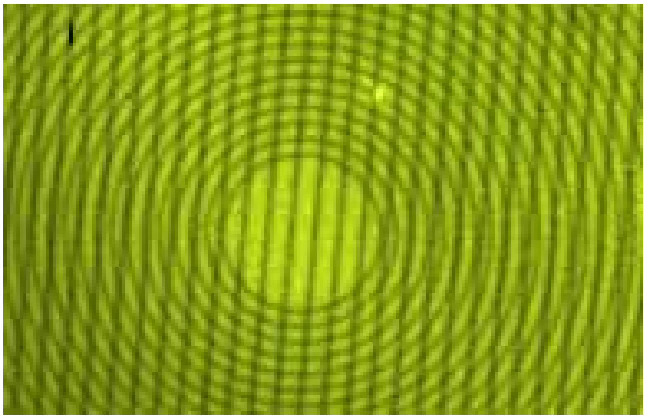

Figure 3. A Photograph of the patterned fluorescent image obtained from photo masked irradiation of the polymer film (line width= 1 um).

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Biography

Eunkyoung Kim received her BS degree in chemistry from Yonsei University in Seoul (Korea) in 1982, a master's degree in chemistry from Seoul National University in Seoul (Korea) in 1984, and PhD in chemistry from University of Houston in 1990. She worked for Korea Research Institute of Chemical Technology in Daejeon (KRICT) from 1992 to 2004. Since 2004, she has been a professor of chemical engineering at Yonsei University, Seoul, Korea. Her work has primarily focused on the development of functional polymers, including chromogenic polymers, photopolymers, and charge transport issues in polymeric media. She has been appointed as an invited professor at ENS-Cachan and Paris 6 Univ. France. She has been a program committee for SPIE-organic 3D material session, editorial committee (Macromolecular Research), committee member (Korea Polymer Society, optical society of Korea, etc), and senior managing director of Korea Society of Imaging Science and Technology (KSIST).