



Photo-crosslinking and negative-type micropattern formation of a polymeric photobase generator containing phthalimido carbamate groups

Kyu Ho Chae*, Hyo In Cho, Yoo Ho Kim, U Chan Yang

Department of Polymer Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea

ARTICLE INFO

Article history:

Received 27 September 2010
Received in revised form 30 April 2012
Accepted 2 May 2012
Available online 15 May 2012

Keywords:

Photosensitive polymer
Photo-crosslinking
Micropattern
Photobase generator
Photoresist
Phthalimido carbamate

ABSTRACT

The photo-crosslinking reaction of a polymeric photobase generator containing phthalimido carbamate (PC) groups was studied and applied to the formation of a negative type micropattern. The copolymer containing PC groups was prepared through the polymerization of methyl methacrylate and phthalimido methacryloxyethylcarbamate (PMC). The photochemical and cross-linking reaction of the copolymer film were studied using the UV and IR absorption spectral changes along with the normalized thickness measurements upon irradiation. The copolymer film was effectively cross-linked upon irradiation with 254 nm UV light, and the cross-linking reaction progressed further with increasing irradiation dose and the amount of PMC units in the copolymer. The photochemical formation of the isocyanato groups was evidenced by comparing the IR absorption spectral changes of the exposed and masked copolymer film. The photo-crosslinking reaction of the copolymer was further studied by using a model compound. The results indicated that the cross-linking reaction occurred because of the formation of urea-type chemical bonds, which were produced through the reaction of the photochemically produced isocyanato and amino groups in the copolymer. A negative micropattern was obtained by using the photo-crosslinking reaction.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Photobase generators (PBGs) are a group of compounds that produce a base upon irradiation. The chemical systems that produce free amines include carbamates, *O*-acyloximes, formamides, metallocenes, transition metal complexes, ammonium salts, and sulfonamides etc. Recently, new PBGs including amineimides, α -aminoketones, amineimides, nifedipines, and aromatic ureas have been examined and reviewed [1].

PBGs have been applied to photoresists, cross-linking agents for epoxy resin, imidation catalysts, and surface modification, etc. Recently, the use of PBGs has expanded into the development of new technologies. Polymers containing photobase-generating groups have been used to

pattern electroluminescent polymers [2], conductive polyaniline films [3], biomolecules [4,5], and nanoparticles [6]. They have also been applied to the formation of colored patterns [7,8] and fluorescent images [9–11] as well as polymer synthesis [12] and degradation [13].

One advantage of the photobase generating system over the free radical is that the photobase generating system is free from the oxygen inhibition effect from air. The use of the photobase generating system can avoid some disadvantages of the photoacid generating system such as corrosion of metal substrates. It appears that the PBGs will be increasingly applied to develop new technologies.

In a previous work, the photolysis of oxime-urethane derivatives or a polymeric photobase generator containing oxime-urethane groups led to the formation of amines, which induce a cross-linking reaction in an epoxy resin [14–19]. Polymeric photobase generators containing oxime-urethane groups have been used to prepare photoresists [20–22] and image-recording materials [7–10].

* Corresponding author. Tel.: +82 062 530 1874; fax: +82 062 530 1909.
E-mail address: khochoae@chonnam.ac.kr (K.H. Chae).

Additionally, phthalimido carbamates (PCs) are another type of PBGs, and the polymer containing PC groups can be used as a bicolor fluorescent imaging material [9] and a photocuring agent for epoxy resin [19]. The study of the photobase generation from polymers containing PC groups showed that polymer could be cross-linked through the photochemical decomposition of the PC groups. In this work, the photo-crosslinking reaction and negative type micropattern formation of a polymeric photobase generator containing PC groups were examined, and the reaction mechanism for the photo-crosslinking was studied by using a model compound.

2. Experimental

2.1. Materials and instruments

N-Hydroxyphthalimide and isocyanatoethyl methacrylate were obtained from Aldrich and Dow Chemicals Co., respectively. Phthalimido phenylcarbamate (PPC) [23] and phthalimido methacryloxyethylcarbamate (PMC) [9] were prepared using previously reported procedures. Ultraviolet (UV) absorption spectra were obtained with a Jasco V-530 spectrophotometer. Infrared (IR) absorption spectra were taken on a Shimadzu model FTIR-8300 spectrophotometer. ¹H NMR spectra were taken on a Bruker ASX-32 300 MHz spectrometer. The thermal decomposition temperature (*T*_d) was determined using a Mettler thermal analyzer (TGA) Model SDTA851^e at a heating rate of 10 °C/min under a nitrogen atmosphere. Gel permeation chromatography (GPC) was carried out using a Young-in model 910 solvent delivery module that was equipped with Young-lin M720 absorbance detector. Shodex AT-806 and 80 MS columns were used for the molecular weight determination measurements. One module of a Rayonet photochemical reactor (The Southern New England UV Co., model RPR-208), that was equipped with a 254 nm fluorescent lamp was horizontally placed and used to irradiate the polymer films. At 254 nm, a light intensity of 1.89 mW/cm² was measured using a radiometer (Vilber Lourmat Co., model VLX-3W). Mass spectrum was acquired on a hybrid ion-trap time-of-flight mass spectrometer (Shimadzu LCMS-IT-TOF, Kyoto, Japan) equipped with an electrospray ionization source (ESI-IT-TOFMS). A sample solution was prepared by dissolving the sample in a solution of methanol to a final concentration of 50 µg/µL. The micropatterns were observed using a Digital Instruments model Nanoscope IIIA atomic force microscope (AFM).

2.2. Polymerization

The reaction conditions that were used for preparing copolymers are shown in Table 1. The typical polymerization conditions for the preparation of copolymer I are shown below. Methyl methacrylate (0.9 g, 9.0 mmol), PMC (0.32 g, 1.0 mmol), and azobisisobutyronitrile (AIBN) (6.1 mg, 0.5 wt.% of monomers) were dissolved in tetrahydrofuran (THF) (5.0 mL). The THF solution was charged into a cap tube and purged with nitrogen for 20 min. After the cap tube containing the reaction mixture was sealed,

polymerization was carried out at 60 °C for 20 h. The copolymer was isolated by double precipitation from THF solution to methanol and dried under a reduced pressure at room temperature. Yield; 61 % (0.75 g).

2.3. Film preparation

A 10 wt.% copolymer solution was filtered with a 0.45 µm Millipore filter after the copolymer (0.5 g) was dissolved in THF (5 mL). The solution was spin coated on a quartz plate or a silicon wafer that was pre-treated with H₂O₂ and H₂SO₄ to form an oxide layer [24] at 1600 rpm for 10 s and 3200 rpm for 10 s, consecutively. The polymer film on the silicon wafer or the quartz plate was dried at room temperature under reduced pressure. The film thickness was 0.9 µm.

2.4. Normalized thickness

The changes in the normalized thickness were observed as a function of the post exposure baking (PEB) temperature for the copolymer III film. The copolymer III film on a silicon wafer was irradiated with a 254 nm UV light at 0.0, 1.0, or 3.0 J/cm². The irradiated film was post exposure baked at various temperatures for 15 min and the IR absorption spectra of the post exposure baked film were observed. Then the post exposure baked film was dipped into a THF/methanol (10/1, v/v) solution for 3 min. The dipped film on a silicon wafer was dried for 4 h under a reduced pressure at room temperature, and the IR absorption spectrum of the dried film was measured again. The normalized thickness of the copolymer III film was determined from Eq. (1);

$$\text{Normalized thickness} = \frac{\text{Absorbance at } 1743 \text{ cm}^{-1} \text{ after dipping}}{\text{Absorbance at } 1743 \text{ cm}^{-1} \text{ before dipping}} \quad (1)$$

The normalized thickness changes of the copolymer films were obtained as a function of the irradiation doses using the similar procedure as shown above except for the PEB. The copolymer film on the silicon wafer was irradiated with a 254 nm UV light at 1.0 J/cm² intervals. The irradiated film on the silicon wafer was dried at room temperature under reduced pressure, and then the IR absorption spectrum of the dried film was observed. The irradiated copolymer film was dipped in THF/methanol (10:1, v/v) for 3 min, and dried at room temperature under reduced pressure. The IR absorption spectrum of the dried film was observed. The normalized thickness of the copolymer films was determined from Eq. (1).

2.5. Photolysis of PPC

A 0.35 M solution of PPC (1.0 g, 3.5 mmol) in acetonitrile (10 mL) was charged into a quartz tube and purged with N₂ for 20 min. The PPC solution was sealed in the quartz tube and irradiated with a 254 nm UV light for 3 h. The photolysis product of PPC was isolated by the preparative silica gel thin layer chromatography (TLC) using a benzene and ethyl acetate (4:1, v/v) solution as a developing solvent. The

Download English Version:

<https://daneshyari.com/en/article/1399724>

Download Persian Version:

<https://daneshyari.com/article/1399724>

[Daneshyari.com](https://daneshyari.com)