Journal of Photopolymer Science and Technology
Volume 25, Number 4 (2012) 497-499 © 2012CPST

Communication

Synthesis of Photobase Generators Based on Proazaphosphatrane – Tetraarylborate Complex for i-Line Photopatterning

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1. Introduction

Photopolymers are the key technology to support our daily life in a variety fields such as coatings, inks, and photoresists, adhesives, imaging, and stereo-photolithography [1]. A photobase generator (PBG) is a promising photoactive compound in industry [2], but the studies of PBGs are scarce. So far, several types of PBGs were reported such as the cobalt–amine complex [3], *o*-nitrobenzoyl carbamates and urethanes [4], *o*-acyloximes [5], blocked aniline [6], and benzoin carbamate [7] Recently bicyclic guanidium tetraphenylborate complexes as a super-photobase generator (pK_a ~ 26) were synthesized and applied to the formation of photopolymer system for 250 nm photopatterning [8]. Here we report novel PBGs based on proazaphosphatrane (pK_a > 33) and tetraaryl borate complex for i-line photopatterning system.

2. Experimental

2.1 Materials

Diethyl ether and tetrahydrofurane were dried over sodium and distilled prior to use. The epoxy resin (jER-1001) was kindly donated from Mitsubishi Chemical Corporation. The PMA-*co*-PMMA (0.016 : 1) copolymer (M_n ~ 15,000) was purchased from Aldrich. Other solvents and reagents were purchased and used without further purification.

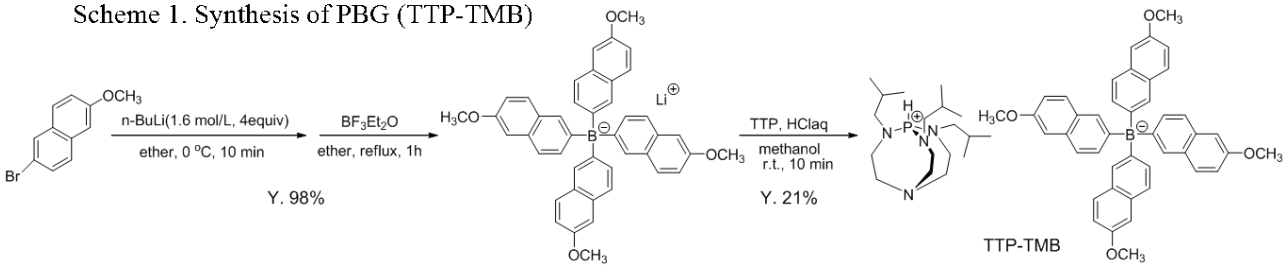
2.2 Characterization

Nuclear magnetic resonance (NMR) was performed on a Bruker AC-400P spectrometer. Uv-vis spectra were recorded on Jasco V-570 UV/VIS/NIR spectrophotometer. The film thickness on silicon wafers was measured by Veeco Instrument Dektak^3 surface profiler.

2.3 Photosensitivity

jER1001 (1.54 g, 80 wt%) and PMA-*co*-PMMA (0.38 g, 20 wt%) were dissolved in THF (20 mL). Into the polymer solution, PBG (5 wt% to the matrix polymers) were added to prepare a photosensitive polymer solution. The solution was dropped onto the silicon wafer, spin-coated at 500 rpm for 10 s, prebaked at 80 ^oC for 5 min, irradiated with 365 nm light for the set time, and

Scheme 1. Synthesis of PBG (TTP-TMB)



Received April 2, 2012
Accepted May 10, 2012

postbaked at 180 °C for 30 min. The film was developed with dry THF for 30 s to make a negative image. A characteristic curve was obtained by plotting a normalized film thickness as a function of exposure dose (mJ/cm^2).

2.4 Synthesis of PBGs (P(*i*-BuNCH$_2$CH$_2$)$_3$N-tetrakis(2-naphthyl borate) (TTP-TMB)

Tetrakis(6-methoxynaphthyl)borate (TMB) (1.1 mmol) was dissolved in water (5 mL). In a dark room, a proazaphosphatrane P(*i*-BuNCH$_2$CH$_2$)$_3$N (TTP) (0.34 g, 1.0 mmol) was dissolved in methanol (10 mL), and the solution was acidified with HCl aqueous solution. Into the solution the borate solution in water was added in one-portion, stirred for 10 min, and the white precipitate was collected by filtration. This was recrystallized from methanol, and dried at 60 °C for 6 h under vacuum to afford the title compound as white plates. Yield 0.094 g (12%), T_m = 144 – 145 °C.

3. Results and discussion

3.1 Synthesis of PBGs

The PBGs were prepared by the lithiation of aryl bromide with n-BuLi, followed by the cation exchange reaction with TTP-HCl complex in water as illustrated in Scheme 1. The compound was characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy.

3.2 Photo absorption

Figure 1 shows the UV-vis spectra of prepared PBGs in DMAc (0.1 mM). The TTP-tetraphenyl borate complex only shows the λ_{max} at 265 nm, and this value is effectively shifted up to 345 nm for TTP-TMB. Although the λ_{max} of the compound is still far from i-line, its absorption edge is on the wavelength. Therefore, we determined to use this compound for the fabrication of a photopolymer system.

3.3 Photolithography evaluation

To check the photobase generation ability of TTP-TMB, the photopolymer was fabricated using epoxy resin (jER1001) and PMA-*co*-PMMA (0.016 : 1) copolymer as the matrix. The detailed procedures are summarized in Figure 2. The polymer mixture was dissolved in THF, and TTP-TMB (ca. 5 wt% to the matrix polymer) was added in a dark room. The solution was spin-coated on a silicon wafer, and prebaked at 80 °C for 5 min, irradiated with 365-nm light for the set time, PEB at 80 to 190 °C for 30 min, and developed with THF for 5s. The suitable PEB temperature to obtain enough dissolution contrast between exposed and unexposed areas was 180 °C. From these results, the photosensitivity curve of the *ca* 1 μm photopolymer film was plotted as shown in Figure 3. In this preliminary experiment, the high sensitivity of 45 mJ/cm^2 and the good contrast of 3.7 were obtained.

Figure 4 depicts the optical microscopic image of the photopatterned film. About 10 μm clear line and space resolution was observed, indicating the high usability of the PBG.

Notably, in the similar photopatterning conditions, Irgacure 907 and DNCDP [9] are both ineffective to obtain a clear photo-image. These results again indicated the high usability of the PBG, TTP-TMB, which generates a super base TTP (pKa > 33) after irradiation of 365-nm industrial standard light.

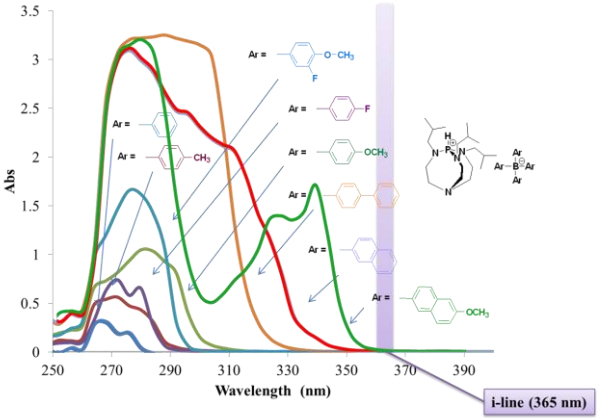


Figure 1. UV-vis spectra of PBGs (1.0×10^{-4}M) in DMAc.

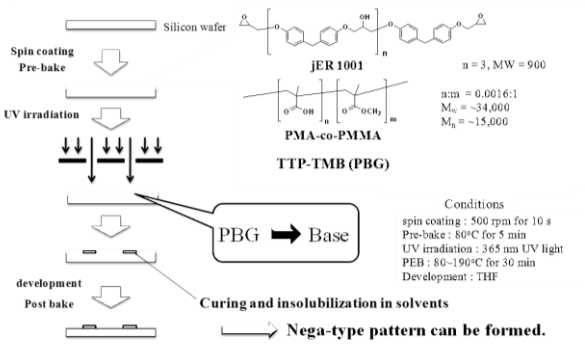


Figure 2. Photopatterning procedures

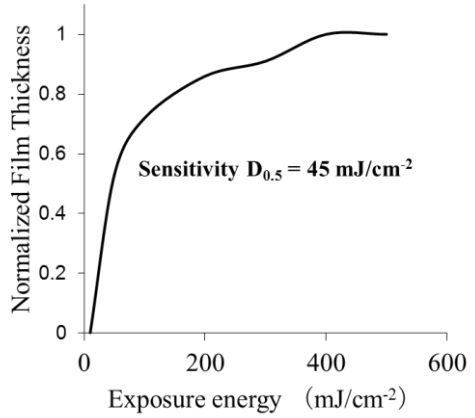


Figure 3. Photosensitivity curve

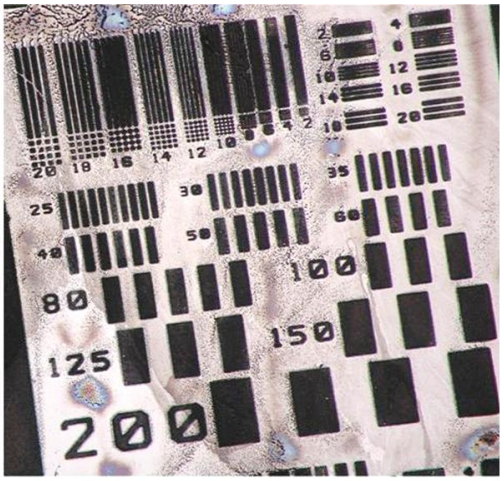


Figure 4. Optical micrograph image fabricated from epoxy resin – PMA-PMMA (20:80). The polymer solution in THF was spincoated at 500 rpm for 10 s, prebaked at 80°C for 5 min, irradiated with 365-nm light at 400 mJ/cm^{-2}, PEB at 180 °C for 15 min, and developed with THF for 10s.

4. Conclusion

We fabricated a novel i-line-photopatternable material based on epoxy resin and $PMA_{0.016}$-*co*-$PMMA_1$ in conjunction with a PBG, (P(*i*-$BuNCH_2CH_2)_3$N-tetrakis(2-naphthyl borate), and demonstrated the preliminary photopatterning experiment using it. The photopolymer system shows a high sensitivity and good contrast of 45 mJ/cm^{-2} and 3.7, respectively. The clear negative-tone image of 10 μm line and space resolution was obtained on a silicon wafer after the irradiation of 365-nm UV light, followed by PEB at 180 °C for 15 min and the development with THF for 10s.

Reference

1. R. W. Peiffer, *ACS Symposium Series*, **673** (1997), 1.
2. K. Suyama, M. Shirai, *Trend. Polym. Sci*., **34** (2009) 194.
3. C. Kutal,C. G. Willson, *J. Electrochem. Soc.*, **134** (1987) 2280.
4. (a) J. F. Cameron, C. G. Willson, J. M. J. Fre´ chet, *J. Am. Chem. Soc*., **118** (1996) 12925. (b) J. F. Cameron, J. M. J. Fre´ chet, *J. Am. Chem. Soc*., **113** (199) 4303.
5. K. Ito, S. Yoshitaka, Y. Kawata, K. Ito, M. Tsunooka, *Can. J. Chem*., **73** (1995) 1924.
6. T. Nishkubo, A. Kameyama, *Polym. J*., 25 (1993) 421.
7. J. F. Cameron, C. G. Willson, J. M. J. Fre´ chet, *J. Chem. Soc*. Perkin Trans. **1** (1997) 2429.
8. X. S. Jian, J. P. Gao, Z. Y. Wang, *J. Am. Chem. Soc*., **130** (2009) 8130.
9. A. Mochizuki, T. Teranishi, M. Ueda, *Macromolecules*, **28** (1995) 365.