

Study on Synthesis and Photochemical Behavior of Carbamate Photobase Generators for Fluorescence Imaging

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ABSTRACT: A fluorescence imaging system is designed based on the photodecomposition of photobase generators embedded in polyvinyl butyral (PVB) matrix. These photobase generators were synthesized with propyl and phenethyl units served as leaving groups, and phthalimido, succinimido, di-2-thienyl ketoximino, and benzophenoneoximino units acted as photosensitive species, respectively. The influences of the two leaving groups and four photosensitive species on the photochemical behavior were investigated in detail. The results demonstrate that the photochemical properties of these photobase generators depend on the photosensitive species other than the leaving groups. And further study shows that succinimido propylcarbamate (SPrC) exhibits the best thermal stability and relatively quick rate of photodecomposition among all the photobase generators. Therefore, a PVB film embedded with SPrC is used as a fluorescence imaging material. The patterned fluorescence image obtained from the fluorescamine-treated irradiated PVB film showed bright green fluorescence, which provides potential application for optical storage or color electronic displays. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41058.

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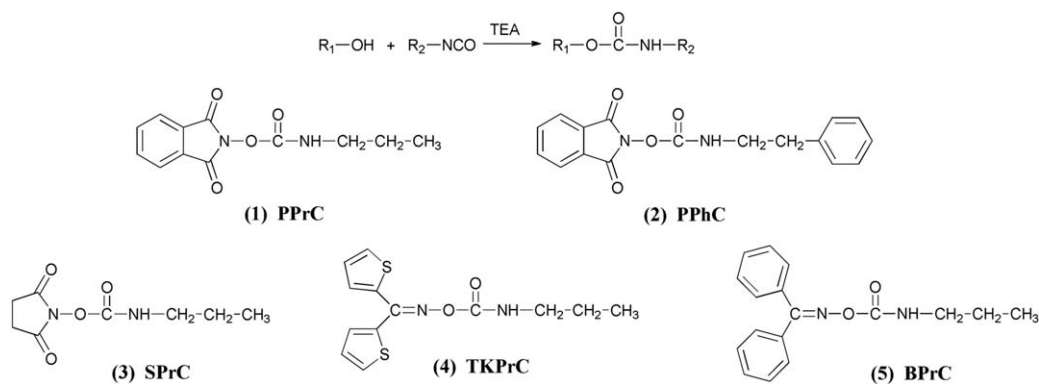
INTRODUCTION

Fluorescence imaging in thin polymer films plays an essential role in both fundamental and applied science. Excellent reviews of luminescent sensors, switch molecules corresponding to various targets,¹ and fluorescence of polymer films by photomasked irradiation for precursors of fluorescent material² have been published. Methods of fluorescence imaging have been widely investigated in biosensor,^{3–7} chemosensor,^{8,9} printing,^{10,11} and other imaging industries. Nowadays, photoirradiation technique represents the most popular and practical approach for fluorescence images generation. The fluorescence imaging in polymer films with this technique can be effectively manipulated by the use of a prefluorescent radical probe,¹² photoinduced oxidative degradation or molecular orientation,¹³ photochromism,^{14–16} photoinduced polymerization,^{2,17,18} and photoacid induced protonation.^{19,20}

Photobase generators are a group of compounds that produce bases upon irradiation.^{21,22} These compounds have been applied as photochemical crosslinking agents for epoxy resins,^{23–26} and also as photoresists,^{27–30} surface modifiers,³¹ and imidation catalysts for poly(amic ester)s.³² However, there are few reports on photobase generating systems for the formation of fluorescence imaging systems comparing with photoradical and photoacid generators. Eun and co-collaborators constructed a film selectively

emitting red, green, and blue fluorescence.² In the system, green-fluorescent fluorescein molecules were encapsulated in red-fluorescent polydiacetylene (PDA) vesicles, and blue-fluorescence component was introduced through the reaction between fluorescamine and the amine groups on the PDA vesicle surfaces. Won et al. reported fluorescence imaging processes based on polymeric photobase generators containing oxime-urethane groups,³³ phthalimido carbamate groups,³⁴ and anilide groups³⁵ through the use of fluorescamine, in which fluorescamine function as the sensitive fluorometric determination of primary amines.

The photobase generating property of photobase generators plays an important role on the formation of fluorescence images. However, to our knowledge there are few reports about the influence of certain property on fluorescence imaging system. Therefore, we designed and synthesized a series of photobase generators with phthalimido, succinimido, di-2-thienyl ketoximino, and benzophenoneoximino units acted as photosensitive moieties, and propyl and phenethyl units served as leaving groups, respectively. The influence of photosensitive moieties and leaving groups on photochemistry characteristics of these photobase generators were deeply addressed by observing their changes in UV-Vis absorption spectra, fluorescence spectra after treatment with fluorescamine and their changes in



Scheme 1. Reaction process for the synthesis of photobase generators with their chemical structures.

pH values. Based on the studies above, succinimido propylcarbamate (SPrC) was chosen to embed in polyvinyl butyral film for the preparation of green fluorescence patterns. This fluorescence imaging material is of potential interest in the preparation of fluorescence images for photonic and optical applications.

EXPERIMENTAL

Materials

N-hydroxysuccinimide (98%) and benzophenone oxime (97%) were purchased from Heowns biochem technologies. Propyl isocyanate (98%) was bought from Tokyo Chemical Industry Bis(2-thienyl) ketoxime (97%) and 2,2'-azo-bis(isobutyronitrile) (AIBN, 99%) were obtained from Alfa Aesar. *N*-hydroxyphthalimide (98%), phenethyl isocyanate (98%), propylene glycol methyl ether acetate (PMA, 99%) and fluorescamine (98%) were purchased from J&K Scientific. Triethylamine (TEA, Analytical reagent, abbreviation for AR), methyl methacrylate (MMA), acetone (AR), cyclohexane (AR), ethanol (AR), and methanol (AR) were supplied by Beijing Chemical Works, and were all used as received. Tetrahydrofuran (THF, anhydrous, AR) was purchased from Heowns biochem technologies and stored in 4 Å molecular sieves. Polyvinyl butyral (PVB, M.W. 90,000–12,000) resin was obtained from Aladdin Industrial Inc. Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh GF254 glass plates.

Synthesis of Photobase Generators

General procedure for the synthesis of photobase generators is similar with the previous report,³³ here we present a simple description. To a solution of R_1 -OH (5 mmol) and TEA (0.03 mL) in THF (50 mL), R_2 -NCO (5.2 mmol) in THF (10 mL) was added drop by drop with stirring at room temperature for 12 h. The structure of R_1 and R_2 are represented in Scheme 1. After the completion of the reaction, the solvent was removed under reduced pressure at 40°C. Crude products were recrystallized from methanol unless otherwise noted.

Phthalimido Propylcarbamate (PPrC). 86% yield. IR (KBr, cm^{-1}): 3307 (N—H stretching), 2979, 2936 (C—H stretching), 1796, 1742 (C=O stretching), 1536 (N—H deforming), 1077, 1029, 975 (phenyl). ¹HNMR (400 MHz, DMSO- d_6): δ = 8.43 (t, J = 5.50 Hz, 1H, NH), 7.98–7.93 (m, 4H, phenyl), 3.09–3.04 (m, 2H, CH₂-CH₂), 1.54–1.45 (m, 2H, CH₂-CH₂), 0.88 (t,

J = 7.38 Hz, 3H, CH₃). DSC: m. p. 186.3°C. Elemental analysis: calc. for PPrC (%), C, 62.90; H, 4.84; N, 11.29; O, 25.81. Found: C, 62.68; H, 4.85; N, 11.23; O, 21.24.

Phthalimido Phenethylcarbamate (PPhC). 75% yield. IR (KBr, cm^{-1}): 3311 (N—H stretching), 2929, 2878 (C—H stretching), 1797, 1764, 1739 (C=O stretching), 1529 (N—H deforming), 978, 692 (phenyl). ¹HNMR (400MHz, DMSO- d_6): δ = 8.56 (t, J = 5.42 Hz, 1H, NH), 7.98–7.93 (m, 4H, phenyl), 7.34–7.22 (m, 5H, phenyl), 3.35–3.30 (m, 2H, CH₂-CH₂), 2.80 (t, J = 7.34 Hz, 2H, CH₂). DSC: m. p. 180.2°C. Elemental analysis: calc. for PPhC (%), C, 65.81; H, 4.52; N, 9.03; O, 20.65. Found: C, 65.92; H, 4.54; N, 8.95; O, 20.59.

Succinimido Propylcarbamate (SPrC). 87% yield. IR (KBr, cm^{-1}): 3329 (N—H stretching), 2971, 2880 (C—H stretching), 1731 (C=O stretching), 1525 (N—H deforming). ¹HNMR (400MHz, DMSO- d_6): δ = 8.26 (t, J = 5.34 Hz, 1H, NH), 3.05–3.00 (m, 2H, CH₂-CH₂), 2.77 (s, 4H, CH₂-CH₂), 1.51–1.42 (m, 2H, CH₂-CH₂), 0.87 (t, J = 7.40 Hz, 3H, CH₃). DSC: m. p. 110.8°C. Elemental analysis: calc. for SPrC (%), C, 48.00; H, 6.00; N, 14.00; O, 32.00. Found: C, 48.16; H, 5.92; N, 13.96; O, 31.96.

Di-2-thienyl Ketoximino Propylcarbamate (TKPrC). 82% yield. IR (KBr, cm^{-1}): 3290 (N—H stretching), 2963, 2934, 2874 (C—H stretching), 1712 (C=O stretching), 1533 (N—H deforming). ¹HNMR (400MHz, DMSO- d_6): δ = 8.06 (d, J = 4.20 Hz, 1H), 7.82 (d, J = 4.40 Hz, 1H), 7.66 (d, J = 3.32 Hz, 1H), 7.60 (t, J = 5.50 Hz, 2H, NH), 7.49 (d, J = 3.16 Hz, 1H), 7.27 (d, J = 4.38 Hz, 1H), 3.10–3.06 (m, 2H, CH₂-CH₂), 1.56–1.46 (m, 2H, CH₂-CH₂), 0.88 (t, J = 7.38 Hz, 3H, CH₃). DSC: m. p. 123.9°C. Elemental analysis: calc. for TKPrC (%), C, 53.06; H, 4.76; N, 9.52; O, 10.88; S, 21.77. Found: C, 53.15; H, 4.73; N, 9.45; O, 11.16; S, 21.51.

Benzophenoneoximino Propylcarbamate (BPrC). 79% yield. IR (KBr, cm^{-1}): 3292 (N—H stretching), 2960, 2933, 2874 (C—H stretching), 1721 (C=O stretching), 1545 (N—H deforming), 764, 697 (phenyl). ¹HNMR (400 MHz, DMSO- d_6): δ = 7.62 (t, J = 5.72 Hz, 1H, NH), 7.57–7.33 (m, 10H, phenyl), 3.09–3.04 (m, 2H, CH₂-CH₂), 1.54–1.45 (m, 2H, CH₂-CH₂), 0.86 (t, J = 7.36 Hz, 3H, CH₃). DSC: m. p. 93.6°C. Elemental analysis: calc. for BPrC (%), C, 72.34; H, 6.38; N, 9.93; O, 11.35. Found: C, 72.49; H, 6.37; N, 9.68; O, 11.46.

Preparation of Fluorescence Patterns

A solution of 5 wt % SPrC embedded in 7.5 wt % PVB was prepared by dissolving 0.25 g SPrC and 0.375 g PVB in 5 mL PMA. The solution was spin-coated onto glasses at 800 rpm for 7 s on the 1st run and at 1500 rpm for 10 s on the 2nd run to form PVB polymer films. The films were dried at 40°C for 1 h under reduced pressure. The thickness of the obtained films ranged from 1.5 to 2 μm . The films on the glass were covered with line/space array photomask and irradiated with 254 nm UV light. The irradiated films on the glass were dipped into a 5.0 mM fluorescamine solution (14.37 mg in 10 mL of a 4 : 1 (v/v) cyclohexane/acetone mixture) for 3 min and subsequently dried at 50°C for 30 min. The patterned fluorescence images were observed through fluorescence microscopy.

Instruments and Measurements

Instruments. Attenuated total reflection fourier-transform infrared spectroscopy (ATR FTIR) was obtained via Pekin Elmer RX1 spectrometer produced by Thermo Corporation at frequencies from 500 to 4000 cm^{-1} . Proton nuclear magnetic resonance (^1H , 400 MHz) spectra were recorded on Bruker AV400 spectrometer using DMSO- d_6 as solvent. Elemental analyses (EA) were carried out on a varioELcube elemental analyzer. Differential scanning calorimetry (DSC) measurements were performed on a TA Q20 system at a heating rate of 10°C min^{-1} under nitrogen atmospheres. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a Hitachi U-3010 spectrophotometer. The relative fluorescence intensity was measured on a Hitachi F-4500 fluorescence spectrophotometer. The thickness of the polymer films was measured using α -step surface profiler (Tencor Instruments, Model AS-500). A Philips lamp (PL-L18W), equipped with 254 nm fluorescent lamp, was used for the irradiation process. The light intensity measured by radiometer was 4.50 mW cm^{-2} . The fluorescence images were observed by Olympus-IX81 fluorescence microscope with exposure time of 5 s.

Measurements for the Absorbance and the Fluorescence Intensity of the Fluorescamine-Amines Adducts

Take PPrC for example, the procedure is as follows. A 0.1 mM solution of PPrC in ethanol was added into a quartz tubes and irradiated with 254 nm UV light. 1 mL of fluorescamine solution (1 mM) in ethanol was added to the irradiated PPrC solution (2 mL) in the quartz tube. After 5 min of reaction, the absorbance was measured and the relative fluorescence intensity at 480 nm was observed upon excitation at 390 nm.

RESULTS AND DISCUSSION

Photochemical Properties of the Photobase Generators

Scheme 1 shows the reaction process for the synthesis of the photobase generators used in our study along with their chemical structures. PPrC and PPhC share the same photosensitive group—phthalimido group, whereas PPrC, SPrC, TKPrC, and BPrC have the same leaving group—propyl group. The photochemical properties of the photobase generators have been studied by observing changes in their UV-Vis absorption spectra upon irradiation, fluorescence spectra after treatment with fluorescamine, and changes in their pH values during the irradiation process.

Figure 1 shows changes in the UV-Vis absorption spectra of the photobase generators in ethanol upon 254 nm UV light irradiation. The absorbance of the photobase generator solutions in ethanol at λ_{max} were adjusted to 0.90–1.10 before irradiation with 254 nm UV light. The final concentrations are 0.6 mM for PPrC and PPhC, 1.2 mM for SPrC, and 0.1 mM for TKPrC and BPrC, respectively. The absorption band at 280–300 nm (PPrC and PPhC), 250–276 nm (SPrC), 245–310 nm (TKPrC), and 230–277 nm (BPrC) decreases upon irradiation owing to the photodecomposition of the carbamate group.^{28,30,33–35} Correspondingly, the band at 300–400 nm (PPrC and PPhC), 276–400 nm (SPrC), 310–400 nm (TKPrC), and 280–400 nm (BPrC) increases upon UV irradiation due to the formation of photo-products. For PPrC and PPhC, the absorption spectra are similar and they have the same decreasing and increasing trends during UV irradiation, which demonstrates their similar photochemical behaviors. This is due to their identical photosensitive group—phthalimido group. However, the other photobase generators with distinct photosensitive groups show totally different photochemical properties comparing with PPrC and PPhC. This result suggests that the photochemical properties of photobase generators depend on the photosensitive groups rather than the leaving groups. As a result, in the following discussion, we only discussed the properties of the four photobase generators with different photosensitive groups: PPrC, SPrC, TKPrC, and BPrC.

The photodecomposition rate of the carbamate group for the four photobase generators can be suggested by the rate constant (k), which is determined from the following equation:

$$k = -\frac{dA}{dt}$$

where A represents the absorbance at 293, 266, 288, and 254 nm for PPrC, SPrC, TKPrC, and BPrC, respectively; t represents the UV exposure time. Figure 2(A) shows the absorbance changes of the four photobase generators at wavelength of A , and Figure 2(B) is their k values at different exposure times. The concentrations for PPrC, SPrC, TKPrC, and BPrC in Figure 2(A) are all 0.5 mM. The k values for the photobase generators follow the order of BPrC > SPrC > TKPrC > PPrC after irradiated for the same time before decreasing to zero. This result indicates that the relative photodecomposition reaction rate of BPrC was the fastest. This seems to be due to the high photosensitivity of the benzophenone group.^{23,28,31} It's worth mentioning that the photodecomposition reactions of PPrC, SPrC, and TKPrC were completed after 400 s irradiation, which correspond to the exposure dose of 1.80 J cm^{-2} . This suggests that the three photobase generators have high photosensitivity.^{25–30}

Figure 3(A) shows UV-Vis absorption spectral changes of fluorescamine solution in ethanol before and after reacting with amino groups coming from the irradiated solution of the four photobase generators in ethanol. Obviously, after reacting with the amino groups, the UV-Vis absorption spectrum of the fluorescamine solution appeared a new absorption band around 390 nm [inset of Figure 3(A)]. Its appearance demonstrates the formation of fluorescamine-amine adducts.^{28,30} Furthermore, Figure 3(B) shows the absorption bands around 390 nm of the four photobase generators as function of UV exposure time.

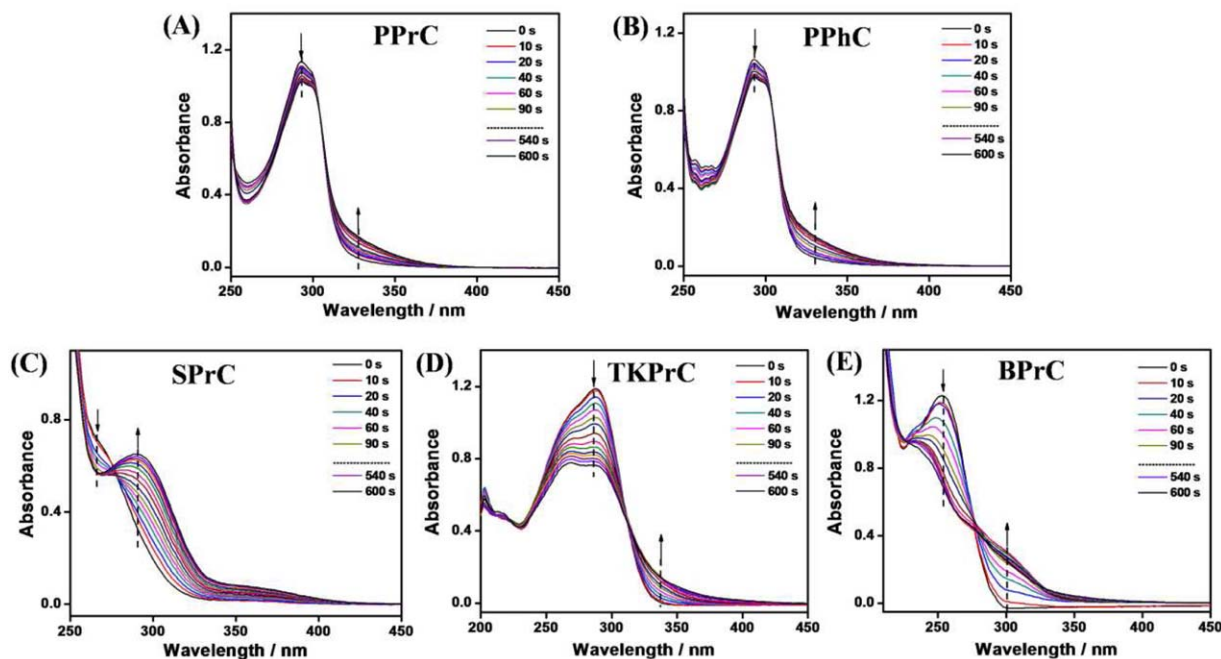


Figure 1. Changes in the UV-Vis absorption spectra of PPrC (A), PPhC (B), SPrC (C), TKPrC (D), and BPrC (E) in ethanol upon irradiation with 254 nm UV light for 0–600 s. The concentrations are 0.6 mM for PPrC and PPhC, 1.2 mM for SPrC, and 0.1 mM for TKPrC and BPrC, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The absorbance of SPrC and TKPrC increase as the irradiation time increasing and reach maximum at 6 and 10 min, respectively, whereas that of PPrC and BPrC increase gradually as the exposure time increasing continually. These changes demonstrate the variety of the concentration of fluorescamine-amine adducts. To discuss the changes of the fluorescamine-amine adducts concentration further and investigate the properties of fluorescamine-amine adducts, fluorescence spectra were carried out.

The fluorescence spectra of the four photobase generators [Figure 4(A)], upon irradiation with 254 nm UV light followed by reaction with fluorescamine, show fluorescence bands in the range of 420–650 nm with a fluorescence maximum at 480 nm.

This result indicates that amino groups are produced upon irradiation, since fluorescamine itself is not fluorescent and only becomes fluorescent after reaction with the amino groups. Figure 4(B) shows the relative fluorescence intensities of fluorescamine treated photobase generator solutions in ethanol at 480 nm as a function of UV exposure time. The fluorescence intensity of PPrC and BPrC increase as the irradiation time increasing and reach their peak at 10 min before gradually decreasing, whereas that of SPrC and TKPrC take 6 min and 10 min to get the maximum respectively, and more importantly keeps stable even irradiated for 30 min. The trends give another evidence for the changes of the fluorescamine-amine adducts

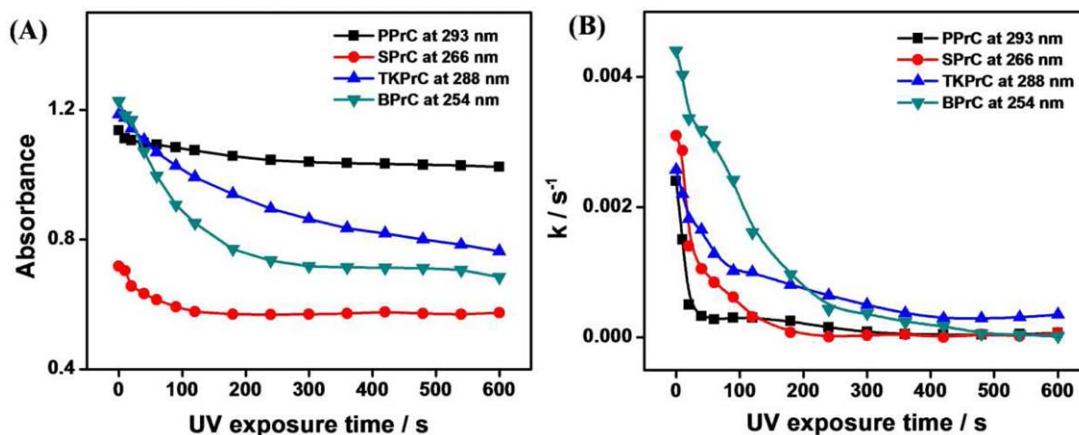


Figure 2. A: Changes in the UV-Vis absorption spectra of the photobase generators at 293, 266, 288, and 254 nm for PPrC, SPrC, TKPrC, and BPrC, respectively, in ethanol with 254 nm UV light irradiation. The concentrations are all 0.5 mM for PPrC, SPrC, TKPrC, and BPrC. B: The k values of the four photobase generators during the UV exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

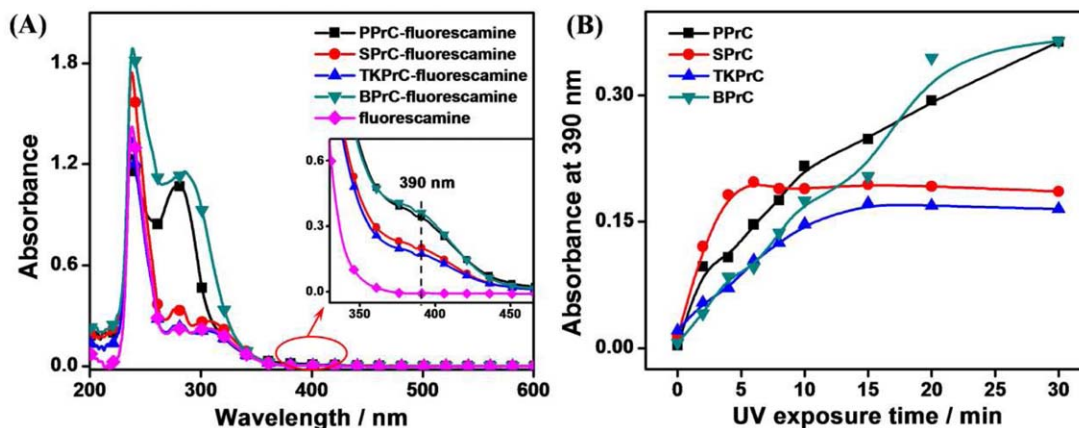


Figure 3. A: UV-Vis absorption spectra of fluorescamine and fluorescamine-amine adduct solutions in ethanol. B: Changes in the UV-Vis absorption spectra of the photobase generators at 390 nm for the four photobase generators after UV irradiation followed by treated with fluorescamine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration. Considering the increase trends of the concentration of fluorescamine-amine adducts in Figure 3(B), the decrease fluorescence intensity for PPrC and BPrC may be due to the self-quenching reaction of the fluorescamine-amine adducts at high concentrations of the amino groups.³⁴ So the relative concentrations of amines from the irradiated photobase

generator solutions can be further studied by observing changes of their pH values.

Figure 4(C) shows the pH changes of a 1 mM ethanol solution of the four photobase generators. The pH values of their solutions increase from ca. 6.2–7.1 to ca. 7.9–8.8 after UV irradiation, suggesting the generation of amines. Self-quenching

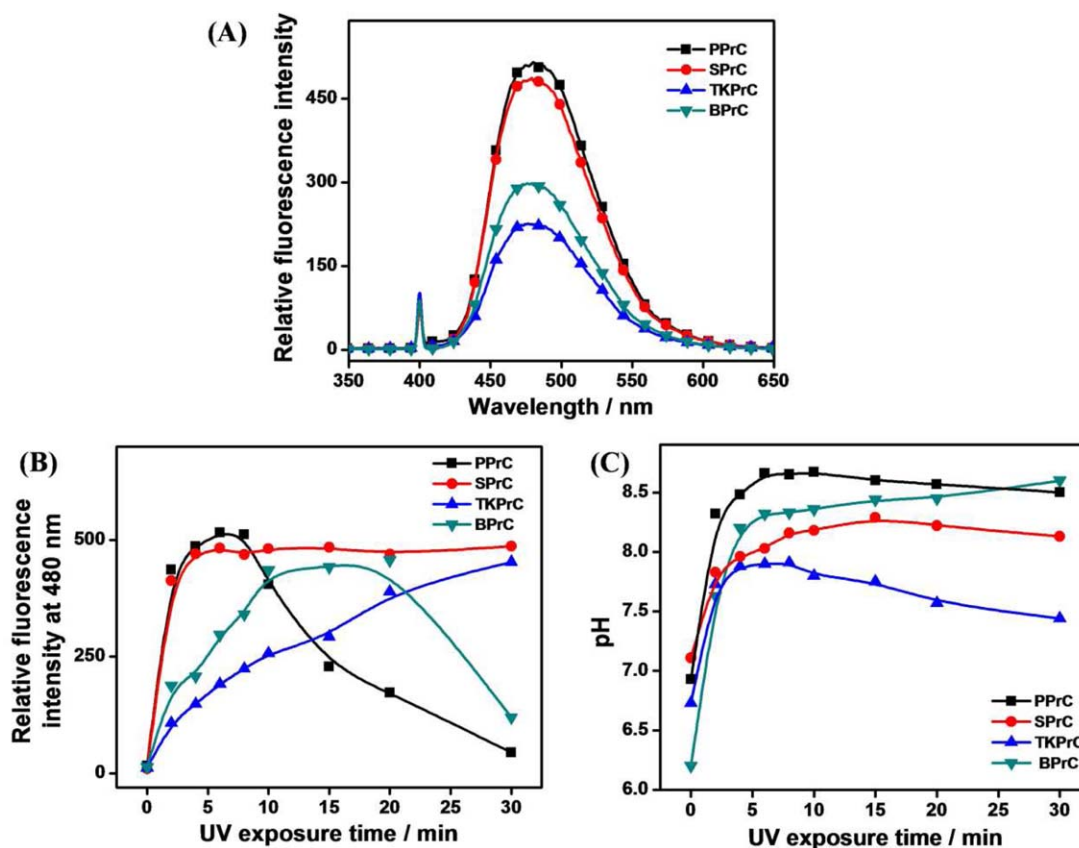


Figure 4. A: Relative fluorescence intensity of the irradiated photobase generator solutions in ethanol after treated with fluorescamine. The irradiation time was 5 min for the four photobase generators. B: Relative fluorescence intensities of the photobase generator solutions after treatment with fluorescamine as a function of UV exposure time. The excitation wavelength is 400 nm and the emission wavelength is 480 nm. C: Changes of the pH values of 1 mM photobase generator solutions in ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

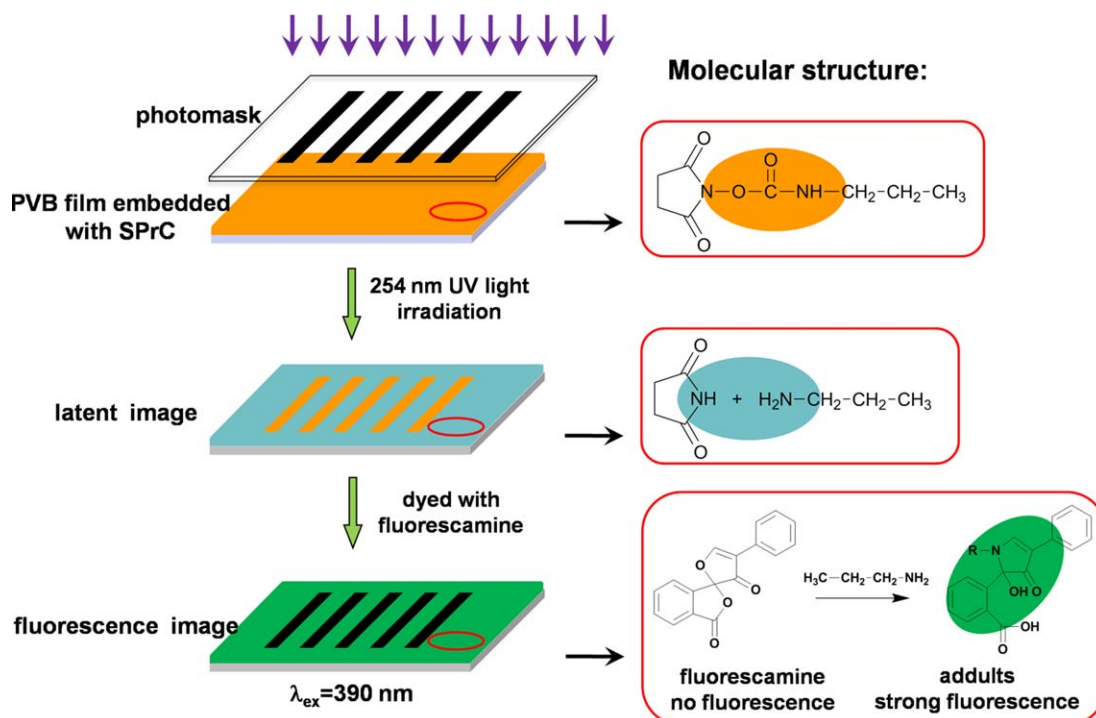


Figure 5. Schematic diagram of the process for the formation of a fluorescence pattern. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

experiments of fluorescamine-amine adducts using alkylamines show that the maximum fluorescence intensity is observed at an alkylamine concentration of 0.1 mM, in which solution the pH value is ca. 8.3–9.0.³⁴ It's worth mentioning that the pH values of PPrC and BPrC solutions are over 8.3, which are in the self-quenching pH value range of the alkylamine. Therefore, the explanation about the decreasing trend for the relative fluorescence intensity of PPrC and BPrC is reasonable.

Fluorescence Patterning Based on Polymer Film Embedded with Photobase Generators

In order to apply the photobase generating properties of the photobase generators to a fluorescence image recording material, a PVB film embedded with SPRC has been prepared. Because of the process for the formation of patterned fluorescence images involves heat treatment procedure, so the thermal stability of the four photobase generators were investigated through thermogravimetric analysis. The decomposition temperatures for the four photobase generators follow the order of SPRC > BPrC > TKPrC > PPrC. This result indicates that SPRC has the best thermal stability among the four photobase generators. Considering its relatively quick rate of photodecomposition further, SPRC was chosen for the patterning experiment. And the use of PVB as the matrix polymer has several advantages that derive from (i) its good compatibility, which allows the incorporation of a variety of molecules; (ii) its ready formulation as a transparency film; and (iii) its alcohol solubility, leading to environmental friendliness; (iv) its inertness towards guest molecules under UV irradiation.

Figure 5 shows a schematic diagram of the process for the formation of patterned fluorescence images. A thin PVB film embedded

with SPRC formed on glass substrate via spin-coating is covered with line/space array photomask and irradiated with 254 nm UV light. A latent image is formed in the irradiated area through the formation of amino groups, which come from the photodecomposition of the SPRC embedded in the PVB polymer film. The consecutive treatment of this latent image with fluorescamine

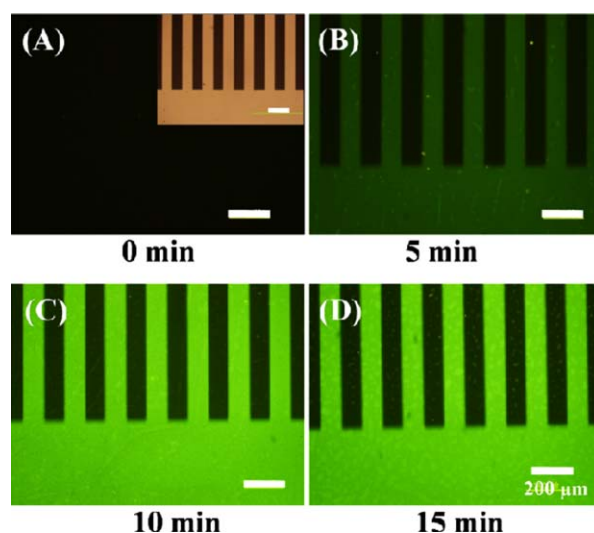


Figure 6. Fluorescence images obtained from the PVB polymer films embedded with SPRC on glasses. The UV exposure time is 0 min (A), 5 min (B), 10 min (C), and 15 min (D). The excitation wavelength is 390 nm. The inset image of (A) is the photomask used for the irradiation process. All the scale bars are 200 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution leads to the formation of dyed image. The dyed image can be observed by fluorescence microscopy.

Figure 6 shows the patterned fluorescence images obtained from the PVB polymer films embedded with SPRc on glasses by the process described above. The image shown in Figure 6(A) has no bright areas since no irradiation was performed through the photomask. Figure 6(B–D) reveals bright green patterned fluorescent images of 100 μm line/space. The bright areas are the portions through the photomask. This result indicates that amino groups are produced upon irradiation, since fluorescamine itself is not fluorescent and it only becomes fluorescent after reaction with the amino groups. In addition, the brightness of the exposed portions in Figure 6(B–D) increased as the UV irradiation time increasing. And patterned fluorescence images with high contrast can be obtained when the film was irradiated for 5 min. The brightness of the exposed portions in Figure 6(C,D) are almost the same, which suggest that the photodecomposition reaction was complete after irradiation for 10 min. The patterned fluorescence images based on our photobase generating system appeared in visible fluorescence with high contrast and resolution under smaller exposure dose comparing with that in literatures.^{28,30,33–35}

CONCLUSIONS

To sum up, a series of photobase generators have been synthesized successfully for fluorescence imaging applications. The photochemical characteristics of the synthesized photobase generators can be adjusted by altering the photosensitive groups. The experimental results indicated by the changes in UV-Vis spectra, fluorescence intensity, and pH values suggest that SPRc has the best property in producing amines upon irradiation with 254 nm UV light among the as-prepared photobase generators. Furthermore, a fluorescence imaging system was designed based on the photodecomposition of SPRc embedded in PVB films. The patterned fluorescence images formed on PVB films show bright green fluorescence. This kind of material may be useful in the preparation of fluorescence images for photonic and optical applications.

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REFERENCES

1. Callan, J. F.; de Silva, A. P.; Magri, D. C. *Tetrahedron* **2005**, *61*, 8551.
2. Park, E. Y.; Kim, J. W.; Ahn, D. J.; Kim, J. M. *Macromol. Rapid Commun.* **2007**, *28*, 171.
3. Gryniewicz, G.; Poenie, M.; Tsien, R. Y. *J. Biol. Chem.* **1985**, *260*, 3440.
4. Suzuki, Y.; Yokoyama, K. *J. Am. Chem. Soc.* **2005**, *127*, 17799.
5. Komatsu, H.; Miki, T.; Citterio, D.; Kubota, T.; Shindo, Y.; Kitamura, Y.; Oka, K.; Suzuki, K. *J. Am. Chem. Soc.* **2005**, *127*, 10798.
6. Weiss, S. *Science* **1999**, *283*, 1676.
7. Seisenberger, G.; Ried, M. U.; Endreß, T.; Büning, H.; Hallek, M.; Bräuchle, C. *Science* **2001**, *294*, 1929.
8. Xu, Z.; Qian, X.; Cui, J. *Org Lett* **2005**, *7*, 3029.
9. Scaiano, J. C.; Laferriere, M.; Ivan, M. G.; Taylor, G. N. *Macromolecules* **2003**, *36*, 6692.
10. Natarajan, S.; Kim, S. H. *Langmuir* **2005**, *21*, 7052.
11. Langowski, B. A.; Uhrich, K. E. *Langmuir* **2005**, *21*, 10509.
12. Coenjarts, C.; García, O.; Llauger, L.; Palfreyman, J.; Vinette, A. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **2002**, *125*, 620.
13. Park, H.; Han, D. C.; Han, D. H.; Kim, S. J.; Lee, W. E.; Kwak, G. *Macromolecules* **2011**, *44*, 9351.
14. Renkecz, T.; Mistlberger, G.; Pawlak, M.; Horváth, V.; Bakker, E. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8537.
15. Lee, J.; Lee, C. W.; Kim, J. M. *Macromol. Rapid Commun.* **2010**, *31*, 1010.
16. Cho, S. Y.; Song, Y. K.; Kim, J. G.; Oh, S. Y.; Chung, C. M. *Tetrahedron Lett.* **2009**, *50*, 4769.
17. Kim, J. M.; Lee, Y. B.; Chae, S. K.; Ahn, D. J. *Adv. Funct. Mater.* **2006**, *16*, 2103.
18. Ahn, D. J.; Kim, J. M. *Accounts Chem. Res.* **2008**, *41*, 805.
19. Lee, C. W.; Yuan, Z.; Ahn, K. D.; Lee, S. H. *Chem. Mater.* **2002**, *14*, 4572.
20. Endo, T.; Suzuki, S.; Miyagawa, N.; Takahara, S. *J. Photochem. Photobiol., A* **2008**, *200*, 181.
21. Shirai, M.; Tsunooka, M. *Prog. Polym. Sci.* **1996**, *21*, 1.
22. Suyama, K.; Shirai, M. *Prog. Polym. Sci.* **2009**, *34*, 194.
23. Chae, K. H. *Macromol. Rapid Commun.* **1998**, *19*, 1.
24. Young, C. J.; Ja, K. T.; Jung, H. M.; Ho, C. K. *Polymer* **1999**, *40*, 4049.
25. Chae, K. H.; Jang, Y. M.; Kim, Y. H.; Sohn, O. J.; Rhee, J. I. *Sens. Actuators, B* **2007**, *124*, 153.
26. Chae, K. H.; Lee, C. S.; Kim, J. H. *Polym. Adv. Technol.* **2011**, *22*, 1427.
27. Suyama, K.; Ozaki, S.; Shirai, M. *React. Funct. Polym.* **2013**, *73*, 518.
28. Chae, K.; Park, J. *Macromol. Res.* **2004**, *12*, 352.
29. Jang, Y.; Seo, J.; Chae, K.; Yi, M. *Macromol. Res.* **2006**, *14*, 300.
30. Chae, K. H.; Cho, H. I.; Kim, Y. H.; Yang, U. C. *Eur. Polym. J.* **2012**, *48*, 1186.
31. Chae, K. H.; Jang, H. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1200.
32. Mochizuki, A.; Teranishi, T.; Ueda, M. *Macromolecules* **1995**, *28*, 365.
33. Choi, W. S.; Noh, Y. Y.; Chae, K. H. *Adv. Mater.* **2005**, *17*, 833.
34. Chae, K. H.; Kim, Y. H. *Adv. Funct. Mater.* **2007**, *17*, 3470.
35. Chae, K. H.; Baek, S. J. *Macromol. Chem. Phys.* **2012**, *213*, 1190.