

Micropatterning of Polymethacrylates by Single- or Two-Photon Irradiation Using π -Conjugated *o*-Nitrobenzyl Ester Phototrigger as Side Chains

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ABSTRACT: A new single-/two-photon sensitive monomer, (*E*)-5-(4-ethoxystyryl)-2-nitrobenzyl methacrylate (ENbMA), was synthesized and copolymerized with methyl methacrylate (MMA) to form a series of photosensitive copolymers P(ENbMA-MMA)s that were well characterized by ¹H NMR and GPC. The photochemical and photophysical properties of both photosensitive monomer and copolymers upon visible light irradiation were studied by UV-Vis, FTIR, and HPLC spectra, which confirmed that 5-(4-ethoxystyryl)-2-nitrobenzyl ester can be photolyzed effectively with generation of the corresponding 5-(4-ethoxystyryl)-2-nitrosobenzaldehyde and carboxylic acid groups. The successful photocleavage endowed the optimized copolymers with excellent micropatterning property due to the effective generation of alkaline-soluble carboxylic acid groups. Moreover, the high two-photon absorption cross-sections (over 20 GM at 800 nm) and the comparable photolysis upon two-photon NIR light irradiation of the chromophores provided the copolymers with significant application in two-photon microfabrication. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4099–4106, 2013

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INTRODUCTION

Stimuli-responsive polymers are capable of exhibiting reversible or irreversible changes in physical properties and/or chemical structures to small changes in external environment. Various types of stimuli, for example, pH, temperature, ionic strength, light irradiation, have been used to induce changes in chain conformation, solubility, and the self-assembly of responsive polymers.¹ Among the stimuli-responsive strategies for polymers, light exhibits significant advantages. It is an external stimulus that could allow a very mild activation of sensitive molecules or chromophores and provides a greater selectivity in terms of control over the moment and the location of polymers. Up to date, considerable efforts have been done for preparing photosensitive polymers, which are used as controllable release or photoresist applications.^{2–4}

Among the reported photoactivated groups, *o*-nitrobenzyl derivatives (ONB) have gained wide acceptance due to their versatile modification and well-known photorearrangement mechanism to generate *o*-nitrosobenzaldehyde.^{3,5–7} Besides its application as an orthogonal protecting group in organic synthesis,⁸ it has been

extensively used in the side chains of polymer as a photochemically labile group and also exhibited utility in photoresist^{9–13} and photocontrolled release in light-dissociable block copolymer micelles.¹⁴ In addition, a lot of caged biological active compounds have been prepared by using ONB phototrigger groups.^{15–20} However, most of the known ONB-caged chromophore showed UV absorption, which is the major drawback and limitation for the practical application, as the presence of UV light provides poor penetration due to light scattering and absorbance by intrinsic polymer chromophores. Recently, Julien and Bolze groups reported that the elongation of the conjugation backbone for the nitro group and the introduction of D- π -A structure would redshift the maximum wavelength of absorption and enlarge the corresponding molar absorption coefficient as well as the two-photon absorption (TPA) cross-sections.^{21,22} We also used the 5-styryl-2-nitrobenzyl (SNB) platform as cage group to prepare a series of prodrugs which exhibited effective photocontrollable release activated either by one-photon visible light or two-photon near infrared (NIR) light.²³

Therefore, inspiring from above research, this article focuses on using SNB ester as phototrigger in the side chain to prepare

photosensitive polymers, which were expected to exhibit excellent micropatterning properties upon visible light irradiation. Herein, as shown in Scheme 1, the methyl methacrylate (MMA) monomer²⁴ was used to copolymerize with a modified (*E*)-5-(4-ethoxystyryl)-2-nitrobenzyl methacrylate (ENbMA), which formed a series of photosensitive copolymers P(ENbMA-MMA)s. The successful controllable photolysis of ENbMA monomer regulated by either one-photon visible light or two-photon NIR laser light endowed the prepared copolymers to serve well as a hopeful positive photoresists as the generated carboxylic acid was soluble in alkaline-developer. In addition, the two-photon activable property of the photosensitive monomer also provided the promising application in two-photon microfabrication.

EXPERIMENTAL

Materials

All reagents were purchased from commercial available sources such as Aldrich, TCI, or Fisher and used without further purification. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Acetonitrile and dichloromethane (CH₂Cl₂) were distilled from calcium hydride before use, and NEt₃ was redistilled from and dried over KOH pellets.

Characterization

Proton and carbon nuclear magnetic resonance spectra (¹H, ¹³C NMR) were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from the SiMe₄ resonance which was used as the internal standard when recording ¹H NMR spectra. Mass spectra were recorded on a Micromass GCTM and a Micromass LCTM. Absorption spectra were recorded on a Shimadzu UV-2550 UV-vis spectrometer. The steady-state fluorescence experiments were performed on a Varian Cary Eclipses fluorescence spectrometer. The molecular weights of polymers were measured by gel permeation chromatography (GPC) using Waters 1515 separation module, and polystyrene was used as a standard with THF as an eluent. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Nicolet 380 FTIR spectrometer on KBr pellets. Thermogravimetric analysis (TGA) was performed under N₂ at a heating rate of 10°C min⁻¹ from room

temperature to 800°C using a NETZSCH STA 409 PC/PG. Differential scanning calorimetry (DSC) was performed under N₂ at a heating rate of 10°C min⁻¹ from room temperature to 180°C and then decreased the temperature to 20°C. The curve was collected at the second heating process from 20°C to 180°C using Shimadzu DSC-60. The morphologies of micropatterning were detected with bright-field microscopy (Nikon-Ti, Co. Ltd., Japan).

General Methods of the Photolysis with Visible and NIR Light

One-photon photolytic reaction of the monomer was performed by irradiating the solution (10⁻⁴ M in acetonitrile) with a CHFXM-500w Xe lamp ($\lambda \geq 400$ nm with power of 30.0 mW/cm²). Between certain time intervals, a small aliquot (20.0 μ L) of the suspension was taken out and analyzed by reversed-phase high performance liquid chromatography (HPLC) using a BetaBasic-18 column eluted with a mixture of 90% acetonitrile and 10% methanol for the monomer in acetonitrile solution at a flow rate of 0.5 mL min⁻¹. The chromatogram was plotted by using absorbance detection at 254 nm. The UV-vis and fluorescence spectra were followed during the HPLC testing.

Characterization of the TPA Cross-section^{25,26}. TPA cross-sections were determined by the method of white continuum Z-scan technique. The 800 nm pump source was from the fundamental of fs mode-locked Ti : sapphire laser system (output beam ≈ 80 fs duration and 250 kHz repetition rate). The laser was focused on a quartz cuvette with a spot size of 1 mm and an optical path length of 10 mm. The sample was dissolved in CH₃CN at a concentration of 10⁻⁴ M. TPA cross-section (δ) was obtained as follows. By assuming a spatially and temporally Gaussian profile for laser beam, the normalized energy transmittance $T(z)$, for two-photon absorption (2PA) can be given as:

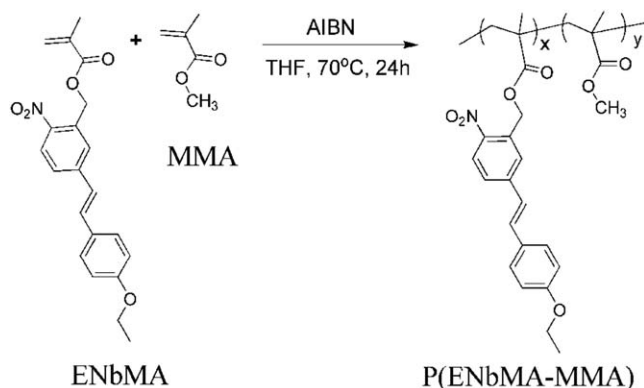
$$T(z) = \frac{1}{\sqrt{\pi}q_0} \int_{-\infty}^{\infty} \ln [1 + q_0 \exp(-x^2)] dx \quad (1)$$

where $q_0 = \beta I_0 L_{\text{eff}}$, β is 2PA coefficient, $L_{\text{eff}} = [1 - \exp(-\alpha l)]/\alpha$, α is linear absorption coefficient, and l is the sample path length. The 2PA coefficient can be obtained by fitting the open aperture Z-scan traces by using eq. (1). From the 2PA coefficient β , 2PA cross-section (δ_{TPA}) can be deduced using the relation $\delta_{\text{TPA}} = h\nu\beta/N_0$, where N_0 is number density of molecules dispersed in the solution.

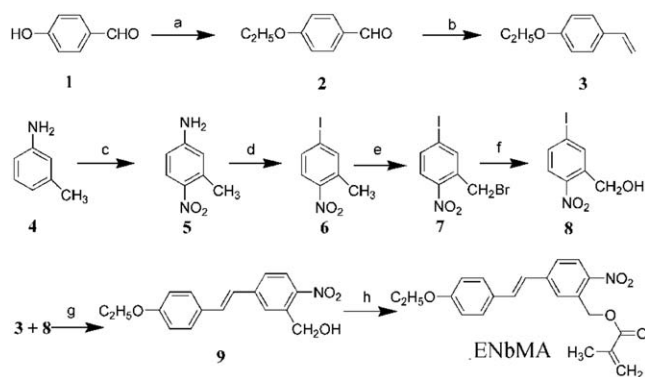
The two-photon photolysis was performed by irradiating with an 80 fs pulses mode-locked Ti : sapphire laser at 800 nm and at a repetition rate of 250 kHz in a quartz cuvette. The NIR beam was focused onto a 2.0 mL monomer suspension placed in a cuvette. With a beam spot diameter of approximately 0.20 mm, the excitation density used for monomer was 0.60 mJ cm⁻² per pulse. The data were collected as described as that for one-photon photolysis.

Monomer Synthesis

Monomer was synthesized according to the route as shown in Scheme 2.



Scheme 1. Structure and synthesis route of copolymers P(ENbMA-MMA).



Scheme 2. Synthetic route of monomer ENbMA. Reagents and conditions: (a) $\text{CH}_3\text{CH}_2\text{Br}$, K_2CO_3 , KI/acetone, reflux overnight, 85%; (b) potassium *tert*-butoxide, methyltriphenylphosphonium bromide/THF, r.t., 71%; (c) guanidinium nitrate/85% H_2SO_4 , 0–5°C, 54%; (d) (1) H_2SO_4 , H_2O , NaNO_2 ; (2) KI, 0 ± 5°C, 90%; (e) NBS, BPO/CCl_4 , reflux, 51%; (f) acetone/ H_2O = 3/1, reflux, 64%; (g) 4-ethoxybenzaldehyde (3), $\text{Pd}(\text{OAc})_2/\text{triethanolamine}$, 100°C, 30%; (h) methacryloyl chloride, $\text{Et}_3\text{N}/\text{CH}_2\text{Cl}_2$, 0°C, 85%.

4-Ethoxybenzaldehyde (2). 4-Hydroxybenzaldehyde (4.9 g, 40 mmol), potassium carbonate (8.3 g, 60 mmol), potassium iodide (166 mg, 1 mmol), bromoethane (5.45 g, 50 mmol), and 100 mL acetone were added into a 250 mL three-necked flask. The mixture was stirred under argon for reflux overnight. After the solution cooled to room temperature, it was filtered to remove the inorganic solids. The excess of acetone was distilled off under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate, 8/1) to afford a colorless oil 2. The yield: 5.1 g (85%). R_f 0.53 (SiO_2 , ethyl acetate/hexane, 1/3, v/v); ^1H NMR (400 MHz, CDCl_3 , δ): 9.88 (s, 1H, CHO), 7.83 (d, J = 8.4 Hz, 2H; Ar H), 6.99 (d, J = 8.4 Hz, 2H; Ar H), 4.12 (q, J = 6.9 Hz, 2H; CH_2), 1.46 (t, J = 6.9 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, CDCl_3 , δ): 190.77, 163.96, 131.89, 129.58, 114.60, 63.81, 14.52; EIMS (m/z (%)): 150.1 (100) [M] $^+$.

1-Ethoxy-4-vinylbenzene (3). To a stirred suspension of 2 (1.5 g, 10 mmol) and methyltriphenylphosphonium bromide (4.28 g, 12 mmol) in dry THF (50 mL), potassium *tert*-butoxide (2.25 g, 20 mmol) was added under argon purge at room temperature. After stirring overnight, the organic layer was washed three times with brine, dried over Na_2SO_4 , filtered, and concentrated. The crude product was purified by silica gel column chromatography (hexane/ CH_2Cl_2 , 20/1, v/v) to afford a colorless oil 3. Yield: 1.05 g (71 %). R_f 0.36 (SiO_2 , CH_2Cl_2 /hexane, 1/6, v/v); ^1H NMR (400 MHz, CDCl_3 , δ): 7.31 (d, J = 8.7 Hz, 2H; Ar H), 6.82 (d, J = 8.7 Hz, 2H; Ar H), 6.63 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H; $\text{CH}=\text{}$), 5.58 (d, J = 17.6 Hz, 1H; $\text{CH}_2=\text{}$), 5.09 (d, J = 10.8 Hz, 1H; $\text{CH}_2=\text{}$), 3.99 (q, J = 7.0 Hz, 2H; CH_2), 1.38 (t, J = 7.0 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, CDCl_3 , δ): 158.83, 136.36, 130.34, 127.48, 114.52, 111.54, 63.53, 14.29; EIMS (m/z (%)): 148.1 (100) [M] $^+$.

3-Methyl-4-nitroaniline (5). To a well-stirred mixture of *m*-toluidine (1.07, 10 mmol) in sulfuric acid (85%, 15 mL), guanidine nitrate (1.22 g, 100 mmol) was slowly added while maintaining the temperature at 0–5°C. After the addition of

guanidine nitrate was completed, the mixture was stirred for an additional hour at the same temperature. The reaction mixture was poured into the ice-cold NaOH solution (20 wt %, 1000 mL). The solid obtained was filtered, washed thoroughly with water, and dried. The finally obtained brown solid was purified by silica gel column chromatography (hexane/ CH_2Cl_2 , 1/2, v/v) to afford a yellow solid 5. Yield: 0.82 g (54%). R_f 0.66 (SiO_2 , ethyl acetate/hexane, 1/1, v/v); ^1H NMR (400 MHz, CDCl_3 , δ): 8.02 (d, J = 8.7 Hz, 1H; Ar H), 6.49 (dd, J_1 = 8.7 Hz, J_2 = 3.7 Hz, 1H; Ar H), 6.47 (s, 1H, Ar H), 4.23 (s, 2H, NH_2), 2.59 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ): 154.44, 154.36, 137.33, 136.20, 128.29, 115.36, 111.07, 22.12; EIMS (m/z (%)): 152.1 (100) [M] $^+$.

4-Iodo-2-methyl-1-nitrobenzene (6). Yellow powder 5 (7.6 g, 50 mmol) was added to conc. H_2SO_4 (98%, 15 mL) and H_2O (150 mL) with mechanical stirring. The resulting solution was rapidly cooled to 0°C and then diazotized at 0–5°C with NaNO_2 (3.8 g, 55 mmol) in H_2O (15 mL). After stirring for 15 min at 0°C, a stirred solution of KI (12.4 g, 75 mmol) in H_2O (35 mL) was added at this temperature within 10 min. The mixture was stirred at 0°C for another 30 min and at r.t. for 3 h, which was followed by extraction with ethyl acetate. The combined organic layer was washed with dilute sodium thiosulfate aqueous solution, brine, and water, dried over anhydrous Na_2SO_4 , and concentrated in vacuum. The crude was purified by silica gel column chromatography (hexane/ CH_2Cl_2 , 10/1, v/v) to afford a white powder 6. Yield: 11.8 g (90%). R_f 0.34 (SiO_2 , CH_2Cl_2 /hexane, 1/4, v/v); ^1H NMR (400 MHz, CDCl_3 , δ): 7.74 (d, J = 8.5 Hz, 1H; Ar H), 7.69 (s, 1H, Ar H), 7.68 (d, J = 8.5 Hz, 1H; Ar H), 2.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3 , δ): 141.58, 136.12, 135.48, 130.10, 125.87, 100.65, 20.20; EIMS (m/z (%)): 263.0 (100) [M] $^+$.

2-(Bromomethyl)-4-iodo-1-nitrobenzene (7). White powder 6 (11.1 g, 42 mmol) was dissolved in dry tetrachloromethane (150 mL), then *N*-bromosuccinimide (8.2 g, 46.2 mmol) and benzoyl peroxide (1.0 g, 4.2 mmol) were added under Ar in two-necked round-bottomed flask fitted with a condenser and Ar bubbler. The reaction mixture was refluxed for 36 h. The mixture was allowed to cool to r.t. and then filtered. The solvent was removed in vacuo and the crude product was purified by silica gel column chromatography (hexane/ CH_2Cl_2 , 10:1, v/v) to afford a light yellow solid 7. Yield: 7.3 g (51 %). R_f 0.24 (SiO_2 , CH_2Cl_2 /hexane, 1/4, v/v); ^1H NMR (400 MHz, CDCl_3 , δ): 7.94 (s, 1H, Ar H), 7.84 (d, J = 8.5 Hz, 1H; Ar H), 7.76 (d, J = 8.5 Hz, 1H; Ar H), 4.76 (s, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3 , δ): 147.43, 141.35, 138.85, 134.45, 126.83, 101.17, 28.02; EIMS (m/z (%)): 340.9 (100) [M] $^+$.

(5-Iodo-2-nitrophenyl)methanol (8). Solid 7 (3.1 g, 9.0 mmol) was dissolved in acetone/water (60 mL, 3:1, v/v) and refluxed for 48 h, then the solution was allowed to cool to r.t. and extracted with ethyl acetate. The organic phase was washed twice with water and brine and dried over Na_2SO_4 . The excess solvent was removed in vacuo. The residual product was purified by silica gel column chromatography (hexane/ethyl acetate, 6/1, v/v) to afford a pale white powder 8. Yield: 1.6 g (64 %). R_f 0.51 (SiO_2 , ethyl acetate/hexane, 1/3, v/v); ^1H NMR (400

MHz, DMSO- d_6 , δ): 8.18 (s, 1H, Ar H), 7.91 (d, J = 8.5 Hz, 1H; Ar H), 7.81 (d, J = 8.5 Hz, 1H; Ar H), 5.64 (t, J = 5.6 Hz, 1H; OH), 4.79 (d, J = 5.6 Hz, 2H; CH₂); ¹³C NMR (100 MHz, DMSO- d_6 , δ): 146.60, 140.75, 137.27, 137.03, 126.48, 103.33, 5.93; EIMS (m/z (%)): 278.9 (100) [M]⁺.

(E)-(5-(4-Ethoxystyryl)-2-nitrophenyl)methanol (9). Under Argon protection, an oven-dried, two-necked round-bottom flask containing a stirring bar was charged with **3** (1.2 g, 4.3 mmol), **8** (700 mg, 4.7 mmol), Pd(OAc)₂ (11 mg, 0.05 mmol), and triethanolamine (20 mL). The mixture was heated and stirred at 110°C for 12 h under Argon. After cooling to room temperature, diethyl ether (2 × 30 mL) was added to extract the product. The combined organic layers were washed with water and brine, dried with Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/hexane, 1/8, v/v) on silica gel to afford a pale white powder **9**. Yield: 1.6 g (64 %). R_f 0.33 (SiO₂, ethyl acetate/hexane, 1/3, v/v); ¹H NMR (400 MHz, CDCl₃, δ): 8.13 (d, J = 8.6 Hz, 1H; Ar H), 7.80 (s, 1H, Ar H), 7.53 (d, J = 8.6 Hz, 1H; Ar H), 7.48 (d, J = 8.7 Hz, 2H; Ar H), 7.25 (d, J = 16.2 Hz, 1H; CH=), 6.99 (d, J = 16.2 Hz, 1H; CH=), 6.91 (d, J = 8.7 Hz, 2H; Ar H), 5.01 (d, J = 6.6 Hz, 2H; CH₂), 4.07 (q, J = 7.0 Hz, 2H; CH₂), 2.58 (t, J = 6.6 Hz, 1H; OH), 1.43 (t, J = 7.0 Hz, 3H; CH₃); ¹³C NMR (100 MHz, CDCl₃, δ): 159.72, 145.37, 144.05, 137.83, 133.21, 128.82, 128.55, 127.08, 126.05, 125.44, 123.88, 114.88, 63.67, 62.91, 14.89; HRMS (ESI, m/z): [M]⁺ calcd for C₁₇H₁₇NO₄, 299.1158; Found, 299.1161.

ENbMA (monomer). 2-Nitrobenzyl alcohol derivative **9** (800 mg, 2.9 mmol) and methacryloyl chloride (606 mg, 5.8 mmol) were stirred in the presence of triethylamine (880 mg, 8.7 mmol) in 10 mL of dichloromethane at 0°C for 12 h. The mixture was filtered and the solvent was evaporated. The crude product was purified by silica gel chromatography (hexane/ethyl acetate, 5/1, v/v) to afford a yellow solid. Yield: 902 mg (85 %). R_f 0.54 (SiO₂, ethyl acetate/hexane, 1/3, v/v); ¹H NMR (400 MHz, CDCl₃, δ): 8.12 (d, J = 8.6 Hz, 1H; Ar H), 7.61 (s, 1H, Ar H), 7.55 (d, J = 8.6 Hz, 1H; Ar H), 7.47 (d, J = 8.6 Hz, 2H; Ar H), 7.19 (d, J = 16.2 Hz, 1H; CH=), 6.96 (d, J = 16.2 Hz, 1H; CH=), 6.91 (d, J = 8.6 Hz, 2H; Ar H), 6.24 (s, 1H, CH=), 5.68 (s, 1H, CH=), 5.63 (s, 2H, CH₂), 4.07 (q, J = 6.9 Hz, 2H; CH₂), 2.02 (s, 3H, CH₃), 1.43 (t, J = 6.9 Hz, 3H; CH₃); ¹³C NMR (100 MHz, CDCl₃, δ): 166.78, 159.78, 143.66, 135.97, 133.26, 133.22, 128.73, 128.56, 126.60, 126.45, 126.06, 125.48, 123.82, 114.89, 63.67, 63.55, 18.53, 14.89; HRMS (ESI, m/z): [M + K]⁺ calcd for C₂₁H₂₁NO₅, 367.1420; Found, 406.1057.

Synthesis of Homopolymer (P0) and Copolymers P(ENbMA–MMA)s (P1–P4)

Structures and synthesis route of polymers were shown in Scheme 1. A typical polymerization was described as follows (taking **P3** as sample): 735 mg of ENbMA (2.0 mmol) and 3.4 mg AIBN (0.02 mmol [2,2'-azobis(2-methylpropionitrile)]) were placed in a Schlenk flask. After the flask was filled with dry Argon by three vacuum-argon cycles, MMA (200 mg, 2.0 mmol) in 4 mL THF were added. After three freeze pump-thaw cycles, the solution was heated to 70°C for 24 h. Then the reaction solution was precipitated three times in 100 mL of

methanol. After filtration and vacuum drying, P(ENbMA–MMA) (465 mg, 50.3% yields) was obtained as yellow powder.

Preparation of Thin P(ENbMA–MMA)s Films and Evaluations

To increase the adhesion strength, the glass slide was previously treated with Piranha solution for 3 h at 80°C and then baked at 90°C for 3 min. Then a 20 wt % polymer solution in N,N-dimethylformamide (DMF) was spin-coated onto the slides at 1000 rpm for 60 s after being filtered through a syringe filter with a 0.45- μ m pore size. Then the slide was dried at 100°C for 4 h in vacuum. The thickness of the films was around 500 nm. Then the obtained films were irradiated under atmospheric conditions with a Xe lamp with the UV-cut filter (\geq 400 nm). The photoresist films were developed with 2.38 wt % tetramethylammonium hydroxide (TMAH) solution at room temperature for 120 s and rinsed with distilled water, and dried with blowing nitrogen; the morphologies were detected with bright-field microscopy. For the two-photon microfabrication, a film of copolymer **P3** was exposed in the pattern of the target structure at 800 nm with tightly focused (0.6 N.A.) 80-fs pulses from a Ti : sapphire laser (250 KHz repetition rate) at an average power of 40 μ W and a linear scan speed of 1.0 μ m s⁻¹. After irradiation, the film was developed for 2 min in 2.38 wt % TMAH solution at room temperature, and the microstructures were detected by microscopy.

RESULTS AND DISCUSSION

Design and Synthesis of Monomer and Polymers

Thinking about the molecular engineering to extend the maximum absorption wavelength and to increase the molar absorptivity, elongation of the conjugated π -system or an increase in the power of the donor and acceptor groups for ONB was required.^{21–23} The introduction of the stilbene in ONB made them be regarded as an excellent photosensitive group because of their visible light absorption and suitable two-photon sensitivity. The molecular structure and synthetic route of monomer was shown in Scheme 2. Here, simple and unfunctionalized ethoxy-styryl group effectively increased the length of the 2-nitrobenzyl conjugated system, and the introduction of methacrylate provided the photocleavable connection and polymerizable group. The synthesis started from ethylation of 4-hydroxybenzaldehyde to obtain 4-ethylxoxystyrene with high yield (71%), which was used as the first part of starting material for the following Heck coupling reaction to form stilbene. The preparation of the photocleavable ONB group was started from the nitration reaction of *m*-toluidine by sulfuric acid and guanidine nitrate at low temperature. Then diazotization reaction was proceeded to prepare the 4-iodo-2-methyl-1-nitrobenzene (90 %), which was brominated and hydrolyzed to obtain 3-hydroxymethyl-4-nitro-iodobenzene (64 %) as the second starting material for the Heck reaction to synthesize the stilbene system. In the end, the esterification was done in dark. The chemical structure of the ENbMA monomer was confirmed by ¹H NMR, ¹³C NMR, and high resolution mass spectroscopy (HRMS), respectively. In the Experimental section, the ¹H and ¹³C NMR spectra of ENbMA were represented with their peaks assignment. The HRMS value of the monomer agreed well with

the calculated value of ENbMA structure. All the spectroscopic data confirmed the expected structure as shown in Scheme 2.

Beside the homopolymer from ENbMA, to adjust the photo-physical properties of the polymers, second monomer, MMA, was selected to copolymerize with the ENbMA to get a series of copolymers Poly(ENbMA-MMA)s with different percentage of ENbMA (P0-P4) (as shown in Table I). The copolymers were synthesized by free radical polymerization of two monomers with different rates in THF at 70°C for 24 h, initiated by AIBN. The resulting copolymers were purified by three precipitations in methanol and dried in vacuum at 30°C for 24 hours. The fundamental physical properties, such as molecular weights, and polydispersity index, were also listed in Table I. ¹H NMR spectra of all homopolymer and copolymers were performed as shown in Figure 1. The aromatic proton peaks from stilbene groups are easy to be observed at 6–8 ppm. The proton peak for the benzyl CH₂ group appeared at 5.33 ppm. By comparing the integration between methyl groups in MMA at 3.51 ppm and another CH₂ groups 4.07 ppm of ethyl in ENbMA, we can calculate the molar ratio of the two monomers in the copolymers as listed in Table I. The similar results from the feeding and NMR calculation proved that the two kinds of monomers have nearly same polymerization rate and they could be copolymerized easily.

Photosensitivity by Single- and Two-Photon Irradiation

Based on the structure of photosensitive monomer ENbMA, the photochemical reactions of the side chains of polymers might be carried out in two ways. The first one is the photocleavage of the ONB ester group to form *o*-nitrosobenzaldehyde and polymethacrylic acid correspondingly^{21–23}; and the second one is the trans-cis isomerization of the stilbene groups under irradiation.²⁷ The possible photochemical mechanisms were schematically represented in Scheme 3. The detailed photoreactions were studied and confirmed by HPLC, UV-Vis spectra, fluorescence and FTIR spectra, respectively. First, in order to check the kinetics of the photodecomposition process, HPLC analysis was performed for the monomer ENbMA. As illustrated in Figure 2, the peak belongs to monomer at 4.16 min decreased which suggested that the photochemical processes progressed effectively upon the irradiation of visible light ($\lambda \geq 400$ nm, 30 mW cm⁻²). At the same time, a shoulder peak at 4.26 min appeared and decreased with the irradiation time. It may be induced by the trans-cis photo-isomerization of stilbene groups as suggested

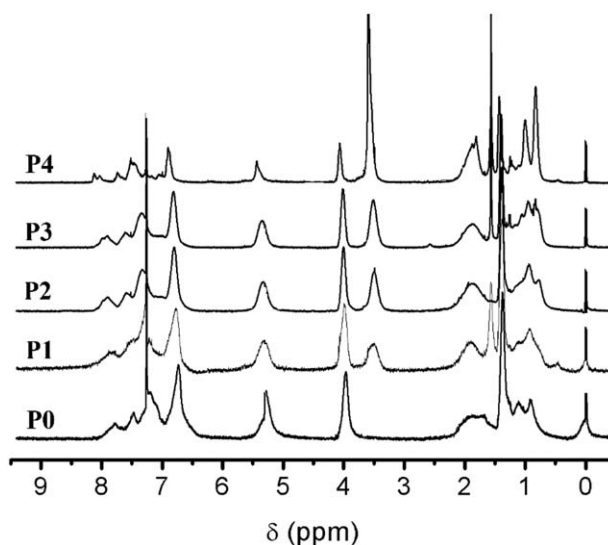


Figure 1. ¹H NMR spectra of P0–P4 in CDCl₃ at 400 MHz.

above. After about 70 min irradiation, the photodecomposition is completed.

For copolymers, taking P3 as example, the photolysis was followed by UV-Vis spectra in acetonitrile. As shown in Figure 3(a), the maximum absorption of the chromophores was located at 382 nm and the absorption band extended up to 475 nm which redshifted about 20 nm comparing with the popular 4,5-dimethoxy 2-nitrobenzyl group, as well as the molar absorption coefficient increased four times.^{21,23,28} It suggested that the introduction of donating power and π -conjugated stilbene prolonged the absorption wavelength and enlarged the molar absorption coefficient, which provided opportunity for the one-photon photodecomposition by visible light. Under visible light irradiation, a rapid decrease in absorbance around 382 nm and an increase in absorbance around 480 nm were indicative of the simultaneous occurrence of the effective photolysis of ONB and isomerization of stilbene groups, as further confirmed by the absence of isosbestic points. However, the UV-vis spectra of irradiated P3 film on quartz showed different phenomenon as shown in Figure 3(b). Compared to the spectra in solution, the peaks at about 480 nm that ascribed to the *cis*-stilbene just increased a little which suggested that the photoisomerization was suppressed in film due to the steric hindrance. Moreover,

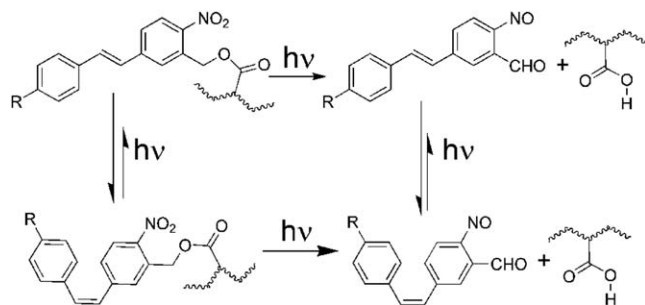
Table I. Experimental Conditions and Results Obtained for Polymerization of ENbMA-MMA^a

Entry	[ENbMA]/[MMA] (feeding ratio)	[ENbMA]/[MMA] (NMR ratio) ^b	Conversion (%)	M_n (g/mol)	M_w/M_n ^c
P0	100/0	100/0	56.9	6600	1.40
P1	67/33	69/31	57.2	6500	1.52
P2	60/40	59/41	55.5	6900	1.61
P3	50/50	49/51	50.3	5200	1.88
P4	25/75	23/77	51.6	5500	1.46

^a The polymerization was performed on a 4 mmol monomer scale in THF at 70°C for 24 h.

^b Calculated by integrity at 4.07 and 3.75 ppm.

^c M_n and M_w/M_n were measured by GPC using a PS calibration.



Scheme 3. Possible photochemical reaction mechanisms for photosensitive chromophore.

the presence of isosbestic points at 243, 269, 326, and 458 nm, respectively, was further indicative of a relative clean photochemical reaction upon visible light irradiation.

In addition, the fluorescence spectra were also compared between the irradiated solution and film, which was similar, and no more useful information could be found as shown in Figure 4(a,b). To prove photolysis reaction did occur, FTIR spectra of film on KBr pellet under irradiation were followed and shown in Figure 5. Upon irradiation with visible light, the signal of the characteristic peaks belonging to NO_2 groups at 1578 cm^{-1} and 1334 cm^{-1} were reduced and a new peak at 1695 cm^{-1} belonging to nitrosoaldehyde and carboxylic acid appeared and increased as a function of irradiation time. It strongly confirmed that the photocleavage of the ONB side chains occurred quantitatively, even in the presence of the photoisomerization as second photochemically induced reaction. This was very important for the following photolithographic evaluation experiments.

The two-photon sensitivity of monomer was also studied and quantified. The δ value was determined at $20 \pm 3\text{ GM}$ by using a 80 fs-pulsed, mode-locked Ti : sapphire laser at 800 nm by the method of white continuum Z-scan technique. Photolysis experiment with two-photon excitation for monomer was measured by HPLC and graphed as a function of irradiation time as shown in Figure 6. It showed that the decomposition was progressed effectively and it reached 30% after 2 h with a $\sim 0.2\text{ mm}$ diameter beam spot. The successful photolysis upon two-

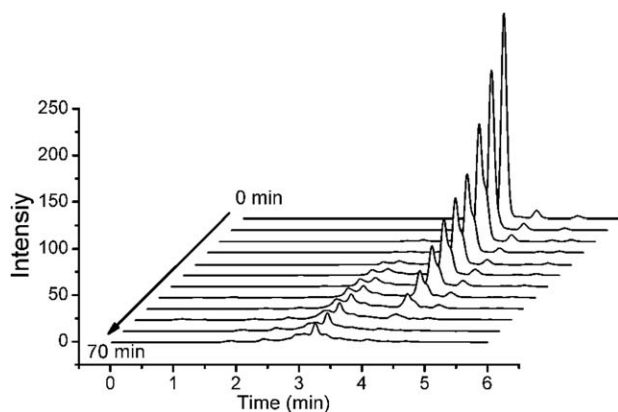


Figure 2. The time course of photodecomposition for ENbMA under visible light irradiation ($\lambda \geq 400\text{ nm}$, 30 mW cm^{-2}) determined by HPLC analysis.

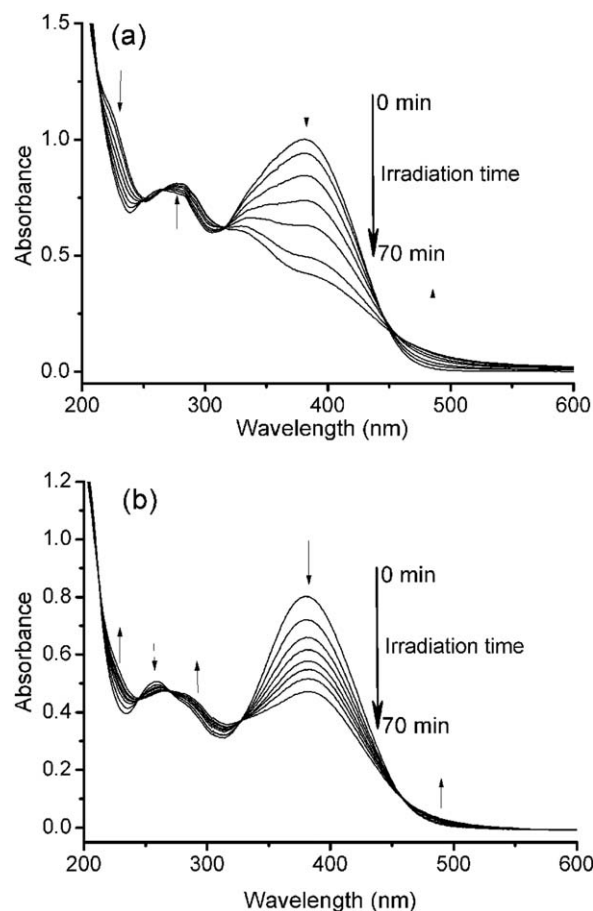


Figure 3. One-photon irradiation ($\lambda \geq 400\text{ nm}$, 30 mW cm^{-2}) of **P3**. (a) Evolution of the UV-vis absorption spectra of the solution in acetonitrile (10^{-4} M) as a function of time (t (min) = 0, 5, 10, 20, 30, 50, 70); (b) Evolution of the UV-Vis spectra of the film on quartz as a function of time (t (min) = 0, 5, 10, 20, 30, 40, 50, 70), the sample was prepared by dropping the solution on a quartz and tested after drying under the vacuum.

photon NIR light irradiation of the photosensitive monomer provided the possibility for the copolymers in two-photon microfabrication application.

Micropatterning

Before studying the possible employment of the copolymers in photoresists and other applications, the thermal properties of polymers were studied by TGA and DSC. As shown in Figure 7, the **P3** showed very good thermal stability below 200°C and its glass transition temperature was 118°C , which was favored the followed photolithography.

As a base-developable photoresist for micropatterning, it is very important to have big enough difference in the solubility in a base developer between the copolymers and their photodecomposed products. For the micropatterning of our copolymers, a 2.38 wt % TMAH solution was exclusively used as a developing solution in the micropatterning field because of environmental reasons. Before visible light irradiation, all copolymers were not soluble because of their hydrophobic properties. However, when the molar ratio of ENbMA was higher than 50% (**P0-P3**), the photodecomposed product would be dissolved by 2.38 wt %

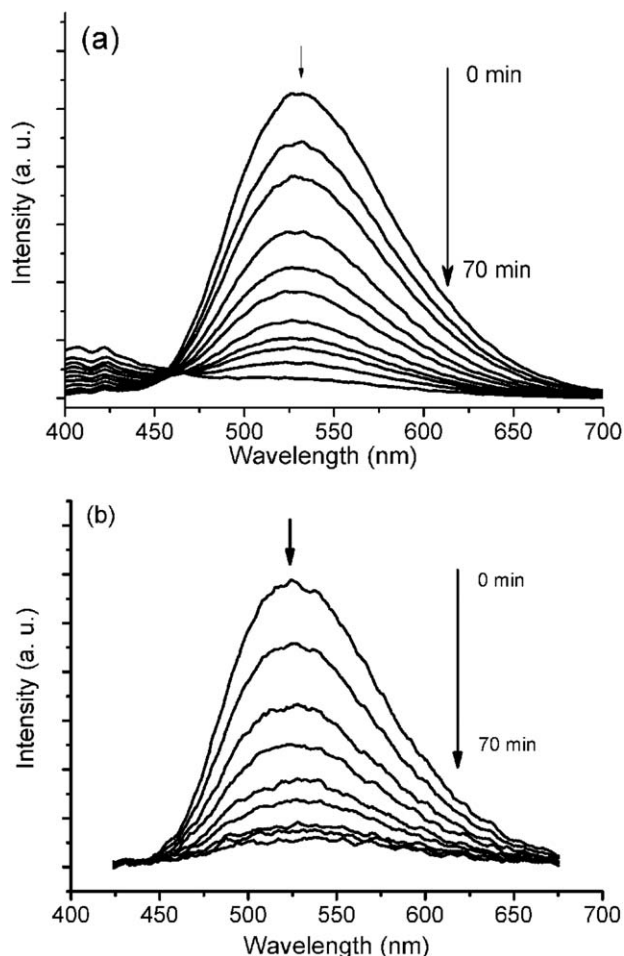


Figure 4. Evolution of the fluorescence spectra of the P3 solution (a) and film (b) as a function of irradiation time ($\lambda \geq 400$ nm, 30 mW cm^{-2} , 0–70 min).

TMAH solution after brief exposure. It suggested that the P(ENbMA–MMA) (P0–P3) would be excellent materials for micropatterning. As shown in Figure 8, taking P3 as sample, a

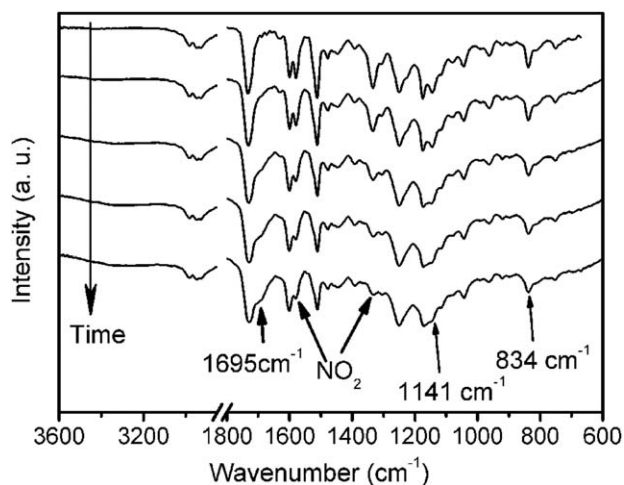


Figure 5. Evolution of the FTIR spectra of the film of P3 as a function of time (t (min) = 0, 10, 25, 45, 70), the sample was prepared by dropping the solution on a KBr pellets and tested after drying under the vacuum.

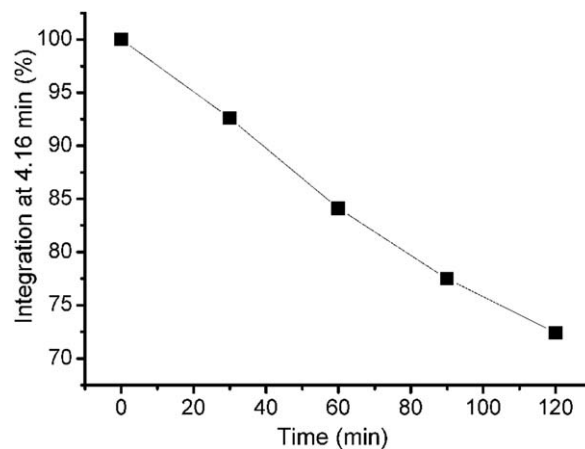


Figure 6. Time course of two-photon decomposition of ENbMA at 800 nm (0.60 mJ cm^{-2} per pulse). Sample (10^{-4} M) was irradiated in acetonitrile solution.

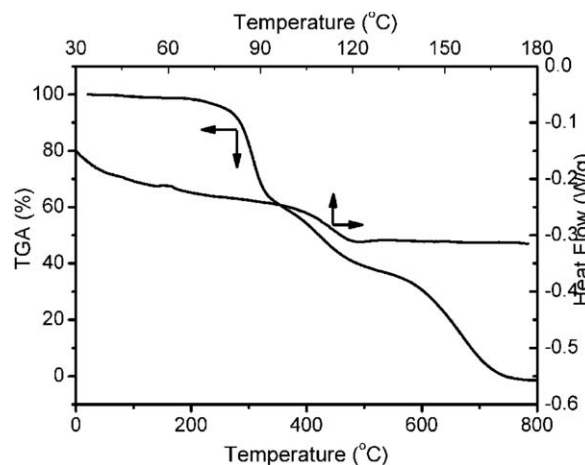


Figure 7. TGA and DSC curves of P3 in N_2 , heating rate: $10^\circ\text{C min}^{-1}$.

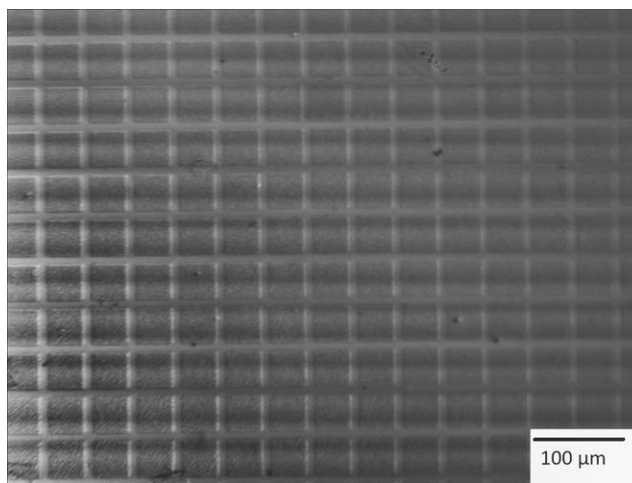


Figure 8. Microscope image by one-photon irradiation ($\lambda \geq 400$ nm, 30 mW cm^{-2}) of film of P3 on Glass slide.

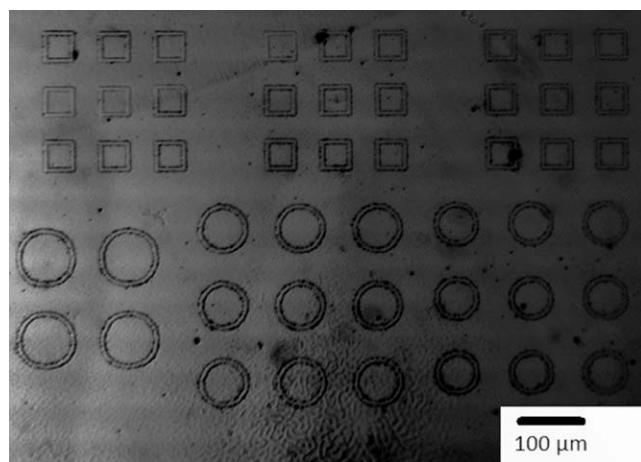


Figure 9. Microscope image by two-photon irradiation ($\lambda = 800$ nm) of film of P3 on Glass slide.

clear photopattern was fabricated and investigated by microscopy after the film was irradiated through a photomask and developed by 2.38 wt % TMAH solution. At the same time, the fs 800 nm laser was also used as the irradiation source to make the two-photon microfabrication, and the micropatterns (such as squares, rings) can be clearly formed after irradiation and development as shown in Figure 9. Before the development, there were no clear patterns and it suggested that they are formed by two-photon lithography, but not by laser ablation.

CONCLUSIONS

In this article, we synthesized a new series of photosensitive polymethacrylate copolymers with a π -conjugated ONB ester as phototrigger side chain. All the spectra characterizations confirmed that both of the monomer and copolymers could be effectively photodecomposed upon either one- or two-photon excitation using visible or NIR light at 800 nm, which avoided the use of UV light and open a new promising way in the applications with long wavelength excitation. The resulted obvious difference in the solubility in a base developer between the copolymers and their photodecomposed products enabled the copolymer realizing the micropatterning application. Combining their considerable two-photon excitable properties, two-photon microfabrication was also realized for these copolymers.

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