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Multifunctional Photodegradable Polymers for Reactive Micropatterns

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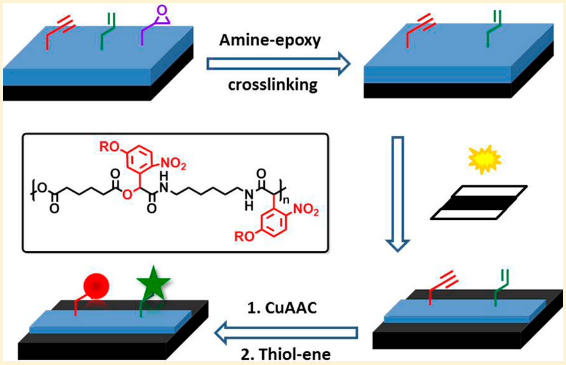
Supporting Information

ABSTRACT: We report the first example of realizing the multi-functionalization of photodegradable polymers for the preparation of reactive micropatterns. Three *o*-nitrobenzaldehyde monomers (**M1**, **M2**, and **M3**) with allyl, propargyl, and epoxy groups were synthesized in high yields by the simple reactions of 5-hydroxy-2-nitrobenzaldehyde with allyl bromide, propargyl bromide, and epichlorohydrin, respectively. Passerini multicomponent polymerization (Passerini MCP) of **M1**, **M2**, or **M3** with 1,6-hexanedioic acid and 1,6-diisocyanohexane generated three poly(ester−amide)s (**P1**, **P2**, and **P3**), the ester linkages of which were *o*-nitrobenzyl derivatives with functional groups from the corresponding monomers. Therefore, these polymers are photodegradable and can also be further modified by efficient click reactions like thiol−ene, copper catalyzed azide−alkyne cycloaddition (CuAAC), and epoxy−amine reaction. Furthermore, Passerini MCP of **M1**, **M2**, and **M3** with 1,6-hexanedioic acid and 1,6-diisocyanohexane could yield a photodegradable triply functional polymer (**P4**) containing all the three functional side groups which can be further modified by sequential click reactions. All the polymers were thoroughly characterized by ^{1}H NMR and GPC. Degradation of the polymers in solution under UV irradiation was investigated by UV−vis and GPC, and they can all be photocleaved into oligomers and small molecules in 30 min. These functional polymers are extremely useful as positive photoresists to create reactive micropatterns. As an example, the triply functional polymer film was fabricated and cross-linked by epoxy−amine reaction. After photoirradiation under a mask, reactive patterns with allyl and propargyl groups were obtained. Sequential modification of the reactive sites by CuAAC and thiol−ene reactions afforded multifunctional patterned surfaces with tunable properties as confirmed by scanning electron micrograph (SEM) and confocal fluorescence microscopy.



■ INTRODUCTION

Recent advances in the area of photodegradable polymers have drawn considerable attention, because light stimulus is especially attractive as it can be remotely applied with high spatial and temporal precision.[1] Various photodegradable polymers with the cleavage linkages in polymer backbones, side groups or junction points have been prepared.[2] Upon irradiation, these polymers could change their structures and subsequent their properties, such as, hydrophobic−hydrophilic balance, electricity, etc., leading to the disruption of materials or release of cargoes. Therefore, they have shown great promise in many applications ranging from controlled drug delivery to surface pattern.[3] Most research efforts have been focused on polymers containing *o*-nitrobenzyl ester units which can cleave themselves into the corresponding *o*-nitrosobenzaldehydes and carboxylic acids upon UV irradiation.[4] However, the syntheses of photodegradable polymers are usually multistep and time-consuming. Recently, we have developed a facile strategy for the synthesis of photodegradable polymers based on Passerini multicomponent polymerization (MCP).[5] This method can produce photodegradable polymers directly from readily available *o*-nitrobenzaldehyde, thus greatly reducing the synthetic steps and expanding the range of applications of photodegradable polymers.

To meet the demand of manifold soft materials, recently, a growing effort has been devoted to introducing multiple functional groups into one polymer scaffold.[6] Thanks to the development of click chemistry, these multifunctional polymers could be designed and synthesized through orthogonal and efficient reactions, which have shown great prospects for a variety of applications of polymers ranging from drug delivery to energy capture.[7] For example, Hawker's group has developed a strategy for independent and orthogonal triple-functionalization of cross-linked polymer thin films through microcontact printing.[8] Khan's group has utilized the amine−epoxy polymerization to prepare polymers with multifunctional groups which

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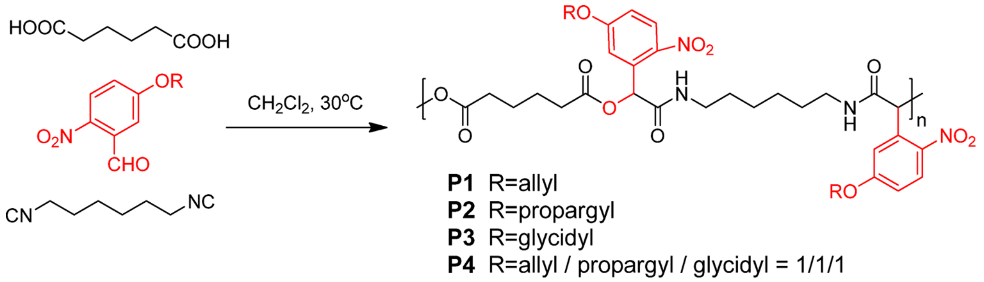
Scheme 1. Synthetic Strategy for the Photodegradable Polymers Based on Passerini MCP



could be further modified through orthogonal click reactions, and these cationic polymers are potential gene delivery carriers with multiple new functions.[9] However, thus far, the reported works are mostly based on passive polymer scaffolds instead of smart ones.[10] In fact, stimulus-responsive polymers have shown tremendous development due to their smart behavior toward various external triggers, such as pH,[11] temperature,[12] enzyme,[13] light,[14] etc. These properties make them good candidates for a wide range of applications including drug delivery, artificial muscles, catalysis, sensors, etc.[15] Therefore, extending the synthetic concept of multifunctionalization to stimulus responsive polymers is both scientifically and technologically important.

Functional photodegradable polymers provide an opportunity for the creation of reactive micropatterns. For example, Ramakrishnan's group has developed a clickable photodegradable hyperbranched polymer to create monofunctional micropatterns which could be modified through copper catalyzed azide−alkyne cycloaddition (CuAAC).[16] Multifunctional photodegradable polymers would provide diverse orthogonal reactive chemical functionalities on the surface to selectively pattern multiple ligands, which may find applications for surface wetting, biomolecules or nanoparticles pattern, etc.[17] Our previous work has demonstrated that Passerini MCP of *o*-nitrobenzaldehyde with 1,6-hexanedioic acid and 1,6-diisocyanohexane is a straightforward way to prepare photodegradable polymers.[5] In order to meet the challenges of multifunctionalization, we proposed that various functional groups (allyl, propargyl, and epoxy) could be introduced into photodegradable polymers by taking the advantage of easily accessible *o*-nitrobenzaldehyde derivatives in the Passerini MCP (Scheme 1). Further modifications could be accomplished by three efficient and orthogonal click reactions. Therefore, these multifunctional photodegradable polymers are excellent scaffolds for constructing multifunctional reactive micropatterns through the classic photolithography technology. To the best of our knowledge, this is the first example of realizing the multifunctionalization of photodegradable polymers.

EXPERIMENTAL SECTION

Materials. 1,6-Hexanedioic acid (>99.5%, Sinopharm Chem. Reagent), 1,6-diisocyanohexane (>98%, Aldrich), allyl bromide (97%; Aldrich), propargyl bromide (80 wt % in toluene, Aldrich), epichlorohydrin (99.85%, Amethyst), 5-hydroxy-2-nitrobenzaldehyde (99%, Beijing DaTianFengTuo Chem. Tech. Co., Ltd.), *n*-dodecanethiol (C.P., Sinopharm Chem. Reagent), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%; Aldrich), morpholine (99.5%, Amethyst), Rhodamine B isothiocyanate (Aldrich) were used as received. Benzyl azide[22] and Azido-FITC[23] were synthesized according to literature methods. CuBr (99.999%; Aldrich) was washed with acetic acid, methanol and ethyl ether and dried in vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN; 98%, Aldrich) was recrystallized twice in methanol. Other reagents were commercially obtained from Beijing Chem. Co. and used without further purification. The silicon wafers were cleaned using piranha solution (H_2O_2/H_2SO_4 = 1/3) and finally washed with distilled water.

Characterization. ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100.5 or 75 MHz) spectra in $CDCl_3$ or DMSO-d_6 were recorded on a Bruker-400 spectrometer or Varian-300 spectrometer. Tetramethylsilane (TMS) was used as the internal reference for chemical shifts (δ, ppm). Polymer characterizations were carried out by different GPC systems. For **P1**, **P1F**, and their degradation products, the M_n and PDI were determined by GPC performed at 35 °C using a Waters 1525 binary HPLC pump connected to a Waters 2414 refractive index detector with THF as the eluent at a flow rate of 1.0 mL/min. For other samples, the M_n and PDI were measured by GPC performed at 50 °C using a SSI pump connected to a Wyatt Optilab DSP differential refractometer detector with DMF containing 0.02 M LiBr as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibrations. UV−vis spectra were recorded on a Shimadzu 2101 UV−vis spectrometer in a 1 cm quartz cell. UV-exposure experiments were conducted under the Spectroline SB-100P/F high-intensity UV lamp (100 W, 365 nm). All the samples were put on a platform at a distance of 5 cm under the UV lamp. Pattern images were observed on a field-emission scanning electron microscope (JEOL JSM-7500F, Japan). The patterns were also imaged using a Nikon A1R-si laser scanning confocal microscope with the excitation wavelength of 488 nm for Azido-FITC and 543 nm for Rhodamine.

Synthesis of 5-Substituted-2-nitrobenzaldehydes. 5-Allyloxy-2-nitrobenzaldehyde (**M1**), 5-propargyloxy-2-nitrobenzaldehyde (**M2**), and 5-glycidyloxy-2-nitrobenzaldehyde (**M3**) were all synthesized by the reaction of 5-hydroxy-2-nitrobenzaldehyde with the corresponding alkyl halides in DMF catalyzed by K_2CO_3.

Take the synthesis of **M1** as an example. 5-Hydroxy-2-nitrobenzaldehyde (5 g, 30 mmol), DMF (150 mL), K_2CO_3 (4.6 g, 33 mmol) and allyl bromide (5.5 g, 45 mmol) were added into a round-bottom flask, and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over sodium sulfate and concentrated to give **M1** in quantitative yield.

Similarly, **M2** was prepared in quantitative yield according to the above procedure with propargyl bromide as the substrate.

Monomer **M3** was synthesized in 75% yield by the reaction of 5-hydroxy-2-nitrobenzaldehyde with epichlorohydrin in DMF at 80 °C for 24 h. The crude product was purified by silica gel column chromatography (ethyl acetate:petroleum ether = 1:4).

Passerini MCP and Synthesis of Photodegradable Polymers (General Procedure). The monomers, **M1**, **M2**, or **M3** (3 equiv), 1,6-hexanedioic acid (1 equiv), and 1,6-diisocyanohexane (1 equiv) were dissolved in CH_2Cl_2. The concentration of 1,6-hexanedioic acid was kept at 1 mol/L. The mixture was stirred at 30 °C for 4 days. Finally, the reaction mixture was precipitated into diethyl ether for three times and then the collected polymer samples were dried under vacuum overnight to give the corresponding photodegradable polymers (**P1**, **P2**, or **P3**).

The triply functional polymer **P4** was prepared by the Passerini MCP of **M1** (1 equiv), **M2** (1 equiv), and **M3** (1 equiv) with 1,6-

hexanedioic acid (1 equiv) and 1,6-diisocyanohexane (1 equiv). The other polymerization conditions were the same as mentioned above.

Postfunctionalization of Polymers. Postfunctionalization of **P1** via thiol−ene "click" reaction: In a Schlenk tube, the allyl functionalized polymer **P1**, *n*-dodecanethiol (10 equiv, with respect to the pendant ally group), and AIBN (0.55 equiv) were dissolved in a minimum amount of DMF. After three freeze−pump−thaw cycles, the reaction tube was sealed and the mixture was stirred at 80 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2 and precipitated into diethyl ether for three times to give the modified polymer **P1F** in 93% yield.

*Postfunctionalization of **P2** via CuAAC.* In a Schlenk tube, the propargyl functionalized polymer **P2**, benzyl azide (2 equiv per propargyl group), and PMDETA (1 equiv per propargyl group) were dissolved in a minimum amount of DMF. After one freeze−pump−thaw cycle, CuBr (1 equiv per propargyl group) was charged into the tube under nitrogen atmosphere. After three freeze−pump−thaw cycles, the tube was sealed and subjected to 30 °C for 24 h. The mixture was diluted with CH_2Cl_2 and passed through a short Al_2O_3 column. The concentrated residue was precipitated into diethyl ether for three times to give the modified polymer **P2F** in 95% yield.

*Postfunctionalization of **P3** via Amine−Epoxy "Click" Reaction.* A mixture of epoxy functionalized polymer **P3** and morpholine (2 equiv per epoxy group) in a minimum amount of DMSO was stirred at 60 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2 and precipitated into diethyl ether for three times to give the modified polymer **P3F** in 90% yield.

*Postfunctionalization of **P4** via Three Sequential "Click" Reactions.* The reaction order was CuAAC, amine−epoxy, and thiol−ene under similar conditions as described above. The modified polymers were designated as **P4F1**, **P4F2**, and **P4F3**, respectively.

Photodegradation of Polymers. The solutions of polymers in CH_2Cl_2 (1 mL, 0.04 mg/mL) in quartz cells were subjected to UV irradiation for different times. The process was monitored by UV−vis spectra. For GPC measurements, a higher polymer concentration was used (CH_2Cl_2, 1 mL, 1 mg/mL), and the resulting mixture after UV irradiation was concentrated and measured by GPC.

Photopatterning of P4. A mixture of **P4** (20 mg/mL) and diethylenetriamine (0.38 mg/mL) in THF was spin-coated onto silicon wafers (300 rpm, 6 s; 2500 rpm, 30 s). The film was cross-linked for 2 h at room temperature and 40 min at 100 °C. The photopatterning process was conducted by a UV lamp (100W, 365 nm) with a TEM grid as the photomask. The exposure time was 20 min. The wafer was then developed in DMF for 2 s and in acetone for 1 min to reveal the pattern. The pattern was imaged on a scanning electron microscopy.

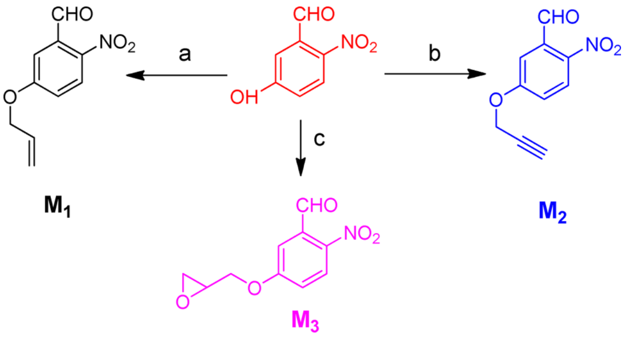
CuAAC Modification of the Patterned Film. Azido-FITC (2 mg), copper(II) sulfate (5 mg), and sodium ascorbate (8 mg) were dissolved in a mixture of DMSO/H_2O (1:9 v/v, 10 mL). The patterned silicon wafer was dipped into this solution and kept at room temperature for 24 h. After washing with DMSO/H_2O (1/9), the FITC modified pattern was examined with a confocal fluorescence microscopy.

Thiol−Ene Modification of the Patterned Film. Cysteamine hydrochloride (150 mg) and $K_2S_2O_8$ (18 mg) were dissolved in a mixture of DMSO/H_2O (1:9 v/v, 5 mL). The FITC modified silicon wafer was dipped into the solution and kept at 60 °C for 24 h. Then the substrate was reacted with Rhodamine B isothiocyanate (16 mg) and triethylamine (20 μL) in DMSO/H_2O (1:9 v/v, 2 mL) for 24 h. After washing with DMSO/H_2O (1/9), the pattern was examined with confocal fluorescence microscopy.

RESULTS AND DISCUSSION

Monomer Synthesis. Our objective was to introduce different clickable side groups into the photodegradable polymers. Previously, we have demonstrated that Passerini MCP of *o*-nitrobenzaldehyde with 1,6-hexanedioic acid and 1,6-diisocyanohexane was an effective way to prepare photodegradable polymers.[5] In this polymerization, *o*-nitrobenzaldehyde was crucial to introduce photodegradable linkages (*o*-nitrobenzyl ester) to the final poly(ester−amide). Thus, it is easy to anticipate that using different *o*-nitrobenzaldehyde derivatives can afford photodegradable polymers with various functional groups. Starting from commercially available 5-hydroxy-2-nitrobenzaldehyde, different functional groups can be easily introduced by the efficient nucleophilic substitution reaction of 5-substituted-2-nitrobenzaldehyde with alkyl halides. Here three clickable groups, allyl, propargyl and epoxy groups, are considered (Scheme 2). Monomers **M1** and **M2** were obtained in quantitative yields after washing with water and evaporating the solvent. Monomer **M3** was prepared from epichlorohydrin at higher temperature (80 °C) in low yield (75%) due to the low reactivity of the epichlorohydrin. The structures of these three monomers were confirmed by ^1H NMR spectra (Figure 1).

Scheme 2. Synthetic Strategy for Functional Monomers from 5-Hydroxy-2-nitrobenzaldehyde[a]



[a] Reagents and conditions: (a) Allyl bromide, K_2CO_3, DMF, room temperature, overnight; (b) Propargyl bromide, K_2CO_3, DMF, room temperature, overnight; (c) epichlorohydrin, K_2CO_3, DMF, 80 °C, 24 h.

Polymer Synthesis and Functionalization. We first introduced allyl groups which are known for thiol−ene click reaction into the photodegradable polymer **P1**.[18] The Passerini MCP of **M1** with 1,6-hexanedioic acid and 1,6-diisocyanohexane (molar ratio of 3:1:1) was carried out in CH_2Cl_2 at 30 °C for 4 days. The purified polymer **P1** was analyzed by ^1H NMR and GPC with THF as the eluent. The ^1H NMR spectrum of **P1** is shown in Figure 2. Analysis of the peaks in the region between 5.2 and 6.2 ppm, corresponding to the alkene protons, clearly demonstrated the successful introduction of the allyl group. Moreover, the appearance of peak c ascribed to the methine of the *o*-nitrobenzyl ester group indicated the existence of the photodegradable linkage in **P1**. The integration ratio of these protons was in accordance with the expected polymer structure. The GPC trace of **P1** displayed a unimodal distribution with a polydispersity index (PDI) of 1.48, and the M_n of 14.3 kDa (Table 1).

P1 was then functionalized with 1-dodecanethiol through thiol−ene click reaction. In principle, this reaction can be conducted either by photoinitiation or by thermal-initiation. Because of the photocleavage property of the polymer backbone, the reaction was carried out with AIBN as the thermal-initiator in DMF at 80 °C. As shown in the ^1H NMR spectrum of **P1F** (Figure 2), the proton resonances of the alkenyl groups disappeared completely, confirming the quantitative functionalization of **P1**. Moreover, the proton signals from the 1-dodecanethiol moiety could be observed in

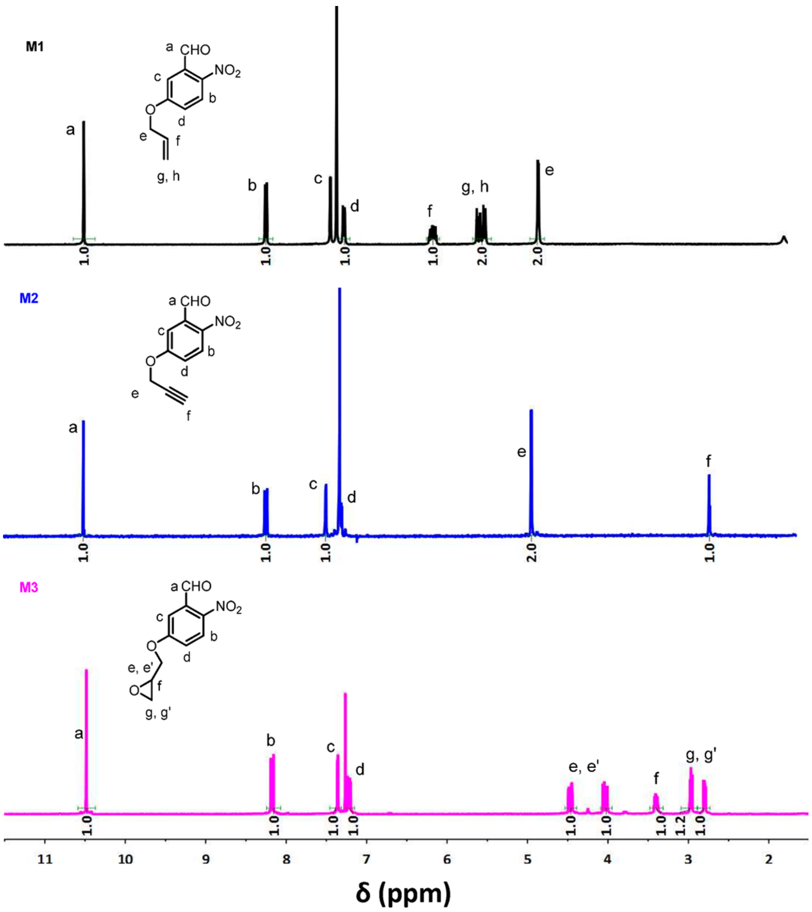


Figure 1. ^{1}H NMR spectra of **M1**, **M2**, and **M3** in $CDCl_3$.

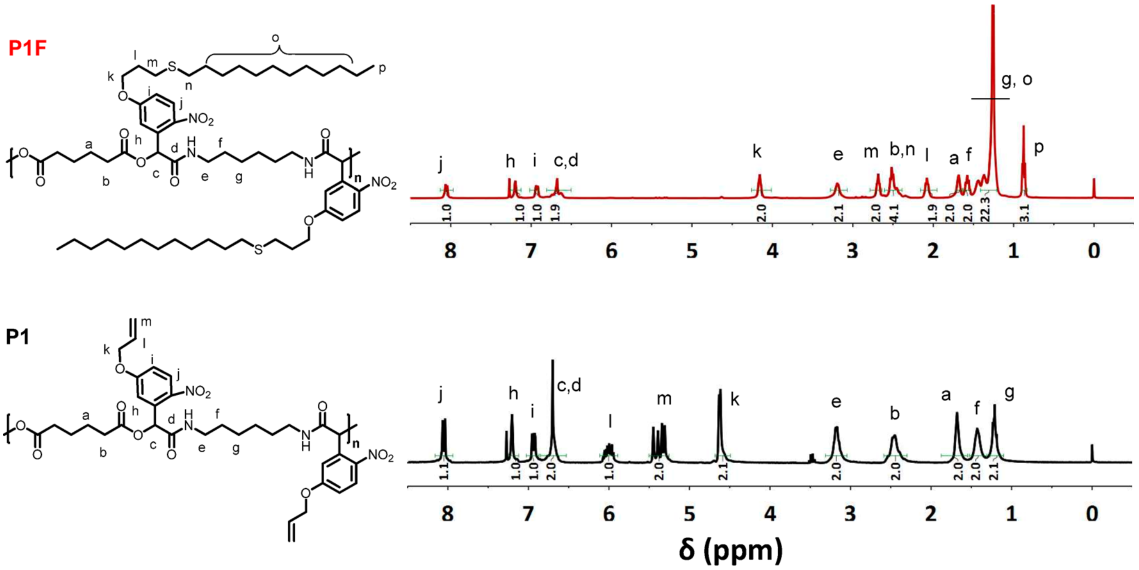


Figure 2. ^{1}H NMR spectra of **P1** and **P1F** in $CDCl_3$.

the range 0.8–1.5 ppm (designated as "o" and "p"). **P1F** has a M_n of 11.0 kDa and a PDI of 1.63 as determined by GPC with THF as the eluent. Collectively, these results have demonstrated that photodegradable polymers with the pendent allyl groups could be prepared by Passerini MCP and further functionalized by thiol–ene click reaction.

We then introduced propargyl groups into polymer **P2**. This group could be modified through CuAAC click reaction.[19] Under the same conditions mentioned above, the propargyl group functionalized polymer **P2** was prepared by the Passerini MCP of **M2** with 1,6-hexanedioic acid and 1,6-diisocyanohexane. The ^{1}H NMR spectrum of the obtained **P2** (Figure S1, Supporting Information) clearly indicated appearance of the

Table 1. Characterization Data for the Polymers

no.	yield/%[a]	M_n/KDa[b]	PDI[b]
P1	87	14.3	1.48
P1F	93	11.0	1.63
P2	80	10.3	1.59
P2F	95	0.8	1.51
P3	95	14.1	1.72
P3F	90	12.6	1.68
P4	88	15.5	1.83
P4F1	87	13.0	1.98
P4F2	95	11.0	1.73
P4F3	90	*c*	*c*

[a] Determined after precipitation into ethyl ether and vacuum dryness. [b] Measured by GPC using THF (for **P1** and **P1F**) or DMF (for other samples) as the eluent. [c] Insoluble in THF, $CHCl_3$ or DMF, partially soluble in DMSO.

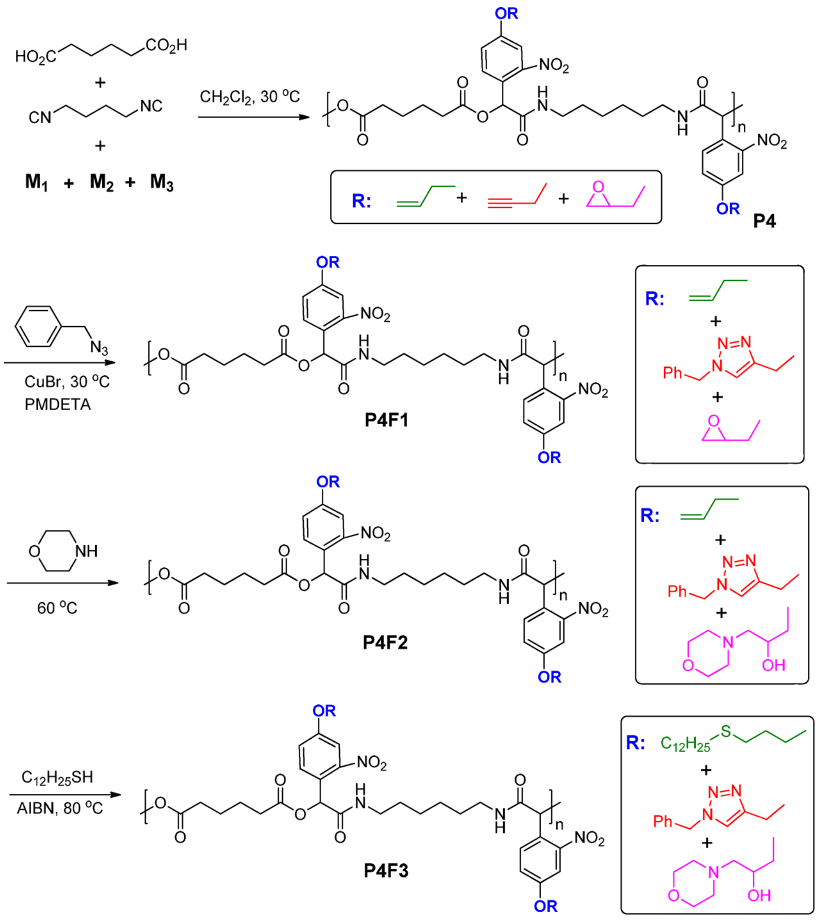
propargyl signals at 2.65, 4.78 ppm and the signal of *o*-nitrobenzyl ester group at 6.73 ppm, and the integration ratio confirmed the integrity of the polymer structure.

P2 was further functionalized with benzyl azide by CuAAC to give **P2F**. The reaction was carried out in DMF with CuBr as the catalyst at room temperature for 24 h. Complete modification could be confirmed by the ^{1}H NMR spectrum of **P2F** (Figure S1). After modification, the peaks of the propargyl groups at 2.65, 4.78 ppm completely disappeared, while the peaks of the benzyl group at 7.30, 7.71 ppm appeared. Besides, all the peaks in the ^{1}H NMR spectrum can be clearly assigned, and the integral ratios are matched well with the theoretical values, confirming the integrity of the polymer structure. **P2** is soluble in THF, but the modified polymer **P2F** is insoluble in THF, for comparison, the M_n and PDI of **P2** and **P2F** were both measured by DMF GPC (Table 1).

To further expand the range of functional groups, another type of photodegradable polymer with pendent epoxy groups were targeted for its easy modification by both amine−epoxy reaction and thiol-epoxy reaction.[20] Epoxy functionalized photodegradable **P3** (M_n = 14.1 kDa, PDI = 1.72, DMF GPC) was obtained by the Passerini MCP of **M3** with 1,6-hexanedioic acid and 1,6-diisocyanohexane. The peaks of epoxy groups at 2.76, 2.91, 3.35, 3.96, and 4.39 ppm and the peaks of *o*-nitrobenzyl ester group at 6.71 ppm were clearly resolved in the ^{1}H NMR spectrum of **P3** (Figure S2), confirmed the polymer structure. For the modification of **P3**, the amine−epoxy click reaction was used because no catalyst was needed in this reaction. To prevent cross-linking, a high reactive secondary amine piperazine was used. The click reaction was conducted in DMSO at 60 °C for 24 h to yield **P3F** (M_n = 12.6 kDa, PDI = 1.68, DMF GPC). Quantitative functionalization was confirmed by the disappearance of peaks of epoxy groups and appearance of piperazine signals (2.53, 3.74 ppm) in the ^{1}H NMR spectrum of **P3F** (Figure S2). Therefore, epoxy functionalized polymers could also be prepared and modified successfully according to our synthetic strategy.

Our final goal is to develop one kind of multifunctional photodegradable polymer. The above results had demonstrated

Scheme 3. Synthetic Strategy for the Photodegradable Triply Functional Polymer P4 and Its Sequential Functionalizations



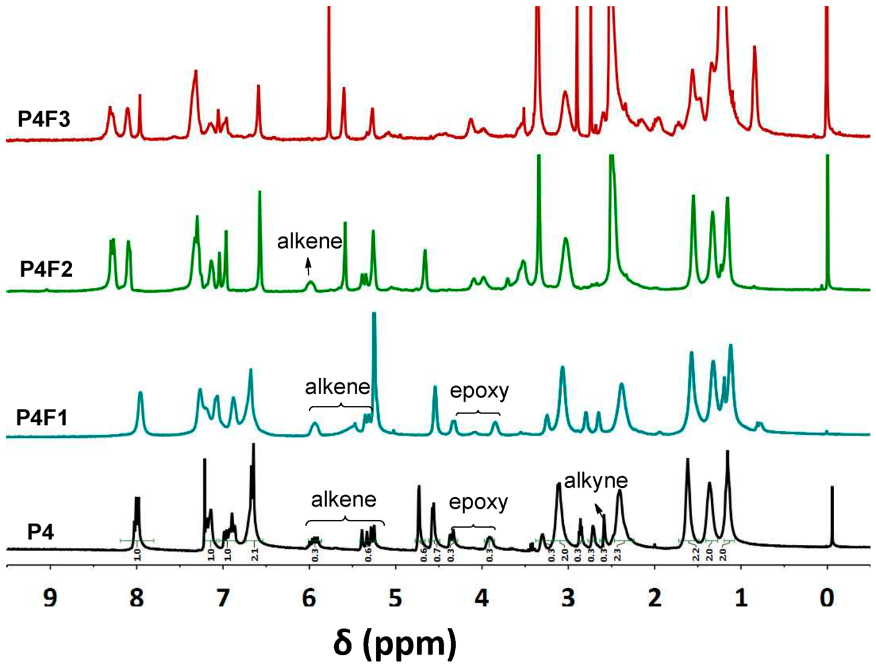


Figure 3. ^{1}H NMR spectra of **P4** in $CDCl_3$, **P4F1** in CD_2Cl_2, **P4F2** in DMSO-d_6, and **P4F3** in DMSO-d_6, respectively.

that allyl, propargyl, and epoxy groups could all be introduced into the polymer by Passerini MCP and further modified through different click reactions. Now, we would try to simultaneously introduce these three functional groups into one polymer and successively functionalize these groups through three sequential click reactions as shown in Scheme 3. Similarly, a mixture of **M1**, **M2**, and **M3** in equal molar ratio was polymerized with 1,6-hexanedioic acid and 1,6-diisocyanohexane to get the photodegradable polymer **P4**. After purification, the obtained polymer **P4** was characterized with ^{1}H NMR and GPC. In the ^{1}H NMR spectrum of **P4** (Figure 3), we could observe the peaks of alkenyl groups (5.28, 5.94 ppm), alkynyl groups (2.65 ppm) and epoxy groups (3.92, 4.37 ppm). Moreover, the integration ratio of these three characteristic peaks was 1:1:1, indicating the equivalent molar ratio of these three functional groups in **P4** backbone. The molecular weight of **P4** was measured by GPC with DMF as the eluent, and the data are summarized in Table 1. Thus, Passerini MCP was a facile approach to triply functional photodegradable polymer.

Polymer **P4** was then functionalized via three successive click reactions, that is, CuAAC, epoxy-amine and thiol−ene reaction (Scheme 3). To ensure independent modification of all the three functional groups, the sequence of click reactions is crucial. On one hand, thiol−ene reaction will occur simultaneously with thiol−yne reaction under the thermal initiation condition; on the other hand, the thiol compounds may also react with epoxy groups at high temperature. Therefore, the thiol−ene click reaction must be conducted last. With this in mind, there are two possible click reaction orders: (1) first CuAAC reaction, followed by epoxy−amine and finally thiol−ene; (2) first epoxy−amine reaction, followed by CuAAC and finally thiol−ene. Here, we choose the first reaction order: **P4** was allowed to react sequentially with benzyl azide, piperazine and 1-dodecanethiol. Each click reaction was conducted under the same condition as that for the modification of **P1**, **P2**, and **P3**. The functionalized polymers after CuAAC, epoxy−amine and thiol−ene are designated as **P4F1**, **P4F2**, and **P4F3**. All the ^{1}H NMR spectra of the modified polymers are shown in Figure 3. As for **P4F1**, the peak of alkynyl groups in **P4** disappeared, while the peaks of benzyl groups appeared at 7.30 ppm. In the ^{1}H NMR spectrum of **P4F2**, the peak of epoxy groups disappeared with the appearance of the peak of piperazine (2.53, 3.35 ppm). Finally, in the ^{1}H NMR spectrum of **P4F3**, the disappearance of the peak of alkenyl groups and the appearance of the peaks of alkyl chain (0.8−1.5 ppm) were clearly observed. Meanwhile, the peak of *o*-nitrobenzyl ester group remained as in polymer **P4**. Besides, all the peaks in these three spectra could be assigned unambiguously and the integration ratio was in accordance with the expected structures. The molecular weights of **P4F1** and **P4F2** were measured by GPC with DMF as the eluent, and the data are summarized in Table 1. Unfortunately, **P4F3** is insoluble in THF, $CHCl_3$, and DMF, which makes it difficult to measure its molecular weight.

Photodegradation of Polymers. The presence of *o*-nitrobenzyl ester group in the polymer main chain endows all these polymers with photodegradable property, because this group can cleave itself into the corresponding *o*-nitrosobenzaldehyde and carboxylic acid upon UV irradiation. We used **P1** and **P1F** as examples to demonstrate the photocleavage behavior of these polymers. The UV-irradiation process was monitored by both UV−vis and GPC measurements. The solution of **P1** in CH_2Cl_2 (0.04 mg/mL) was irradiated with a UV lamp (λ_{max} = 365 nm). As shown in Figure 4A, the absorption peak at 308 nm, ascribed to the *o*-nitrobenzyl ester moiety, decreases with irradiation time and reaches a minimum after 20 min, while new absorption bands appear between 350 and 500 nm due to the formation of the *o*-nitrosobenzaldehyde moiety.[21] GPC traces (Figure 4B) show that the molecular weight decreases gradually with irradiation time. After 2 min, degradation products at high retention time appeared; after 30 min, only oligomers and small molecules existed. Both results confirmed that **P1** could be cleaved by UV irradiation. We also investigated the photocleavable property of **P1F**. Both the UV−vis and GPC results (Figure 4C and 4D) exhibited a similar photocleavable behavior as that of **P1**.

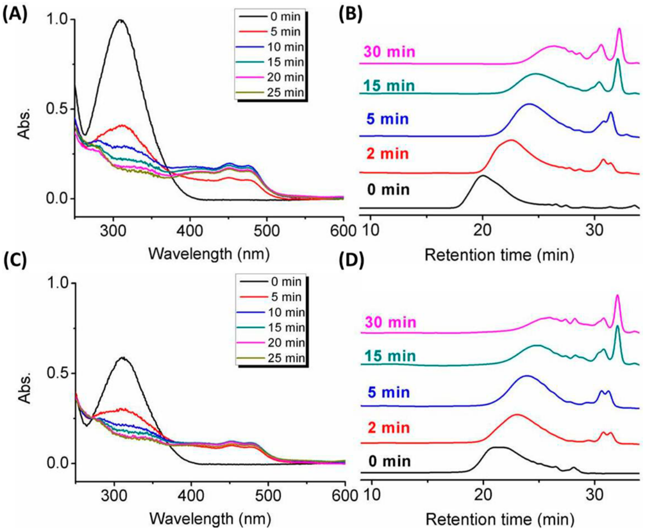


Figure 4. UV−vis absorption spectra of **P1** (A) and **P1F** (C) in CH_2Cl_2 (0.04 mg/mL) recorded as a function of UV exposure time (365 nm, 100 W). GPC traces of **P1** (B) and **P1F** (D) recorded as a function of UV exposure time (365 nm, 100 W) in CH_2Cl_2 (1 mg/mL).

Application for Multifunctional Photoresist. The intrinsic main chain photodegradable property of these polymers could be used as photoresists. Besides, the pendent clickable groups allowed further modification of the patterned surface. We used the triply functional **P4** to examine the possibility as potential photoresist for fabrication of reactive patterns. As shown in Figure 5A, **P4** have four functions: (1) cross-link the photoresist film by amine−epoxy reaction; (2) pattern the surface by the photocleavable property; (3) functionalize the surface by CuAAC reaction; (4) subsequently functionalize the surface by thiol−ene reaction. Consequently, **P4** will create reactive micropatterns for sequential surface modifications.

In an effort to testify to this idea, the mixture of **P4** and diethylenetriamine in THF was spin-coated on a cleaned silicon wafer. The thin films were prepared at 2500 rpm with an acceleration of 100 rpm and duration of 30 s. The film was cross-linked for 2 h at room temperature and 40 min at 100 °C. This amine and epoxy reaction is well-known as the basis for epoxy resins and adhesives.[24] The photopatterning process was conducted by a UV lamp (100 W, 365 nm) with a TEM grid as the photomask. The exposure time was 20 min. The wafer was then developed in DMF for 2s and in acetone for 1 min to reveal the pattern. Figure 5B shows the SEM image of the pattern generated by **P4**, which is consistent with that of the photomask.

To examine the accessibility of alkynyl and alkenyl groups on the **P4** pattern, the patterned substrate was subjected to sequential surface click reactions, that is, CuAAC and thiol−ene reactions. First, the substrate was dipped into the mixture of Azido-FITC, sodium ascorbate and $CuSO_4$ in DMSO/H_2O (1/9). The reaction was conducted at room temperature for 24 h. After washing with DMSO/H_2O (1/9), the patterned substrate was examined with confocal fluorescence microscopy. Figure 5C shows the clear pattern in consistent with the SEM result. Second, the modified substrate was dipped into the DMSO/H_2O solution of cysteamine hydrochloride and initiator $K_2S_2O_8$. The reaction was conducted at 60 °C for 24 h. Subsequently, the substrate was reacted with Rhodamine B isothiocyanate and triethylamine in DMSO/H_2O (1/9) for 24

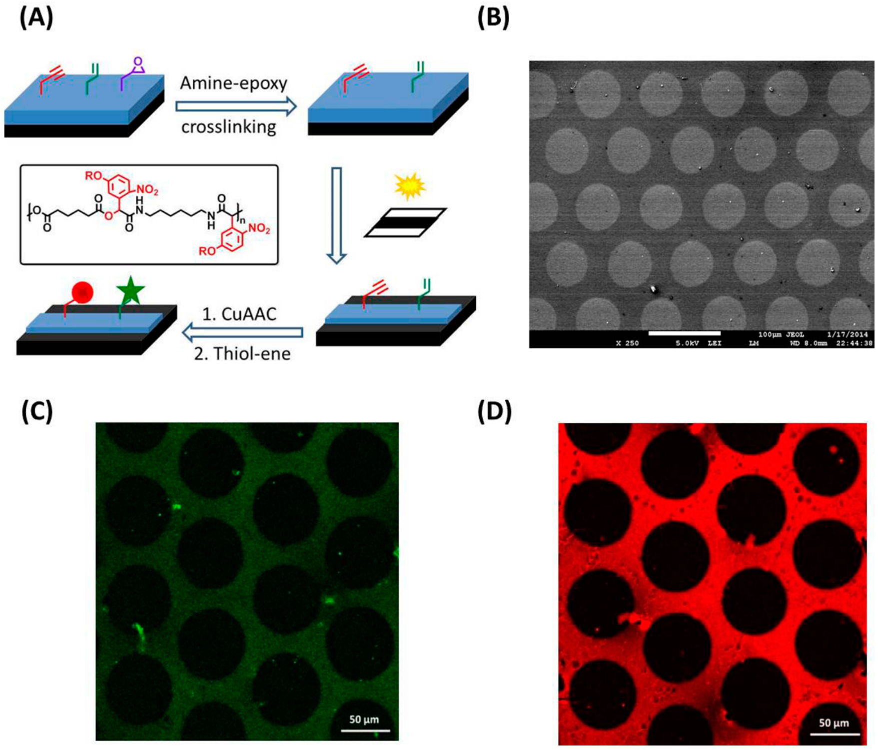


Figure 5. (A) Schematic representation of the process for generation of multifunctional pattern on silicon wafer using **P4** as a photoresist; (B) SEM image of the patterned film (scale bar = 100 μm); confocal fluorescence images of the patterned film functionalized with Azido-FITC (C) and rhodamine dye (D) (scale bar = 50 μm).

h. After this two-step modification, Rhodamine B isothiocyanate was anchored onto the patterned substrate. The confocal image shown in Figure 5D also confirmed the same pattern. Therefore, both SEM and confocal fluorescence microscopy results demonstrated that the triply functional **P4** could create reactive micropattern by sequential click functionalizations.

CONCLUSIONS

A novel family of photodegradable polymers with three different clickable side groups (allyl, propargyl, and epoxy) was prepared by the Passerini MCP of readily accessible reagents. Postpolymerization modifications of these polymers could be accomplished by utilizing click reactions in high conversions. Owing to the presence of *o*-nitrobenzyl ester moieties in the polymer backbone, all these polymers displayed photodegradation behavior under UV irradiation. The triply functional polymer has been demonstrated to be extremely useful as photoresist to create reactive patterns. Thus, the polymer film was cross-linked by epoxy−amine reaction, photopatterned, and the formed patterns were functionalized by sequentially CuAAC and thiol−ene reactions with fluorescent molecules. The facile synthetic strategy and the opportunity for multiple functionalizations of the photodegradable polymers provide great prospects for the development of clickable micropattern for nanoparticles, biomolecules, etc., which are currently being explored in our lab.

ASSOCIATED CONTENT

Supporting Information

^{1}H NMR spectra of **P2**, **P2F**, **P3**, and **P3F.** This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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