Generation of Patterned Color Images in Polymer Film with Photogenerated Base

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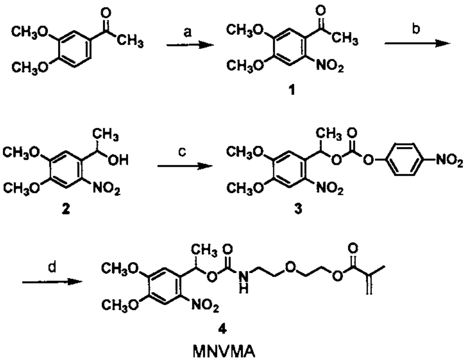
Patterned color images in the polymer film have been prepared using photolabile protecting groups. Irradiation of a polymer film with 360-nm UV through a photomask followed by chemisorption of organic dyes afforded patterned color images in the polymer film.

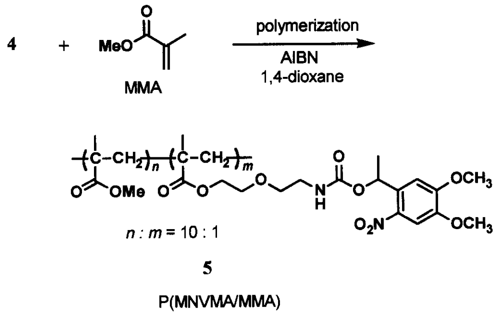
Generation of patterned functional images in polymer films has played very important role in electronic and display industries. Accordingly, many efforts have driven to develop efficient methods for patterned functional images in the polymer films. Recently, the generation of functional images by combination of a chemical amplification (CA) process and a chemisorption of functional dye molecules has been reported.[1–3] Thus, generation of reactive species such as carboxylates or hydroxy groups via CA process followed by interaction with functional dyes have afforded patterned images in the polymer films. Very recently, we also have described novel methods for color and fluorescent functional images by employing intra- or intermolecular hydrogen bonding approach in the polymer film.[4–7] Although the CA process has proven to be very efficient to generate functional groups such as hydroxy or carboxylate in the exposed region of the polymer film, it has intrinsic problems associated with generating more nucleophilic amine moieties since the catalytic amount of acid produced in the first step of CA process would be captured by amine groups and no further catalytic effect would be obtained. Consequently, if amine moieties are desired, direct generation approach using photolabile protecting groups would be more desirable. As part of our ongoing efforts for the development of relief and functional images in the polymer film, we now report preparation of an acrylate polymer having pendant amine groups protected with photolabile protecting groups and application to color imaging.

The strategies employed for the synthesis of α-methylnitroveratryloxycarbonyl (α-MNVOC)-protected acrylate monomer **4** are presented in Scheme 1. Nitration of 3,4-dimethoxyacetophenone followed by reduction with sodium borohydride provided the alcohol intermediate **2**. The intermediate alcohol **2** was converted to an activated carbonate **3**[8] by treatment with 4-nitrophenyl chloroformate. Conversion of the intermediate **3** to the desired monomer **4** was achieved in two steps. Coupling of the activated carbonate **3** with 2-(2-aminoethoxy)ethanol followed by treatment with methacryloyl chloride readily afforded the protected acrylate monomer **4**.[9] The monomer **4** was obtained as pale yellow oil and was fully characterized by spectroscopic analysis.



Scheme 1. Synthesis of α-MNVOC-protected acrylate monomer **4**. a) HNO_3, CH_3COOH, 0 to 25 °C, 3 h, 78%. b) $NaBH_4$, MeOH, 0 to 25 °C, 2 h, 95%. c) 4-nitrophenyl chloroformate, TEA, THF, 25 °C, 2 h, 75%. d) i) 2-(2-aminoethoxy)ethanol, CH_2Cl_2, 25 °C, 2 h; ii) methacryloyl chloride, TEA, THF, 25 °C, 76%, 2 steps.

The 2-(2-aminoethoxy)ethanol linker was introduced between the protecting group and polymerization unit in the monomer **4** to make the resulting polymer both hydrophobic and hydrophilic nature. Copolymerization of the methacrylate monomer **4** having pendant photolabile protecting groups with methyl methacrylate (MMA) was carried out with a 1: 9 molar feed ratio in 1,4-dioxane using 2,2'-azobis(isobutyronitrile) (AIBN) as a radical initiator at 60 °C for 24 h (Scheme 2). The copolymer **5**, P(MMA/MNVMA), after precipitation in *n*-hexane, was obtained as pale yellow powder in 60% yield.



Scheme 2. Preparation of methacrylate copolymer **5** having pendant photolabile protecting groups.

The polymer has an average molecular weight (M_w) of 26000 with compared to a polystyrene standard by gel permeation chromatography (GPC) (polydiversity (PD) = 2.48). The composition of the copolymer obtained was confirmed to have a 1: 10 ratio between the protected monomer and MMA unit by ^{1}H NMR spectroscopic analysis.

In order to investigate the possibility of generation of free amine moieties by photoirradiation,[8] a solution containing the copolymer **5** (10 wt/v%) in 1,4-dioxane was spincoated on a quartz plate with 1500 rpm for 40 s using a Headway spincoater to make a 1.5 mm thick film. The film, then was exposed to UV light (360 nm) and the progress was monitored by UV spectroscopy (Figure 1).

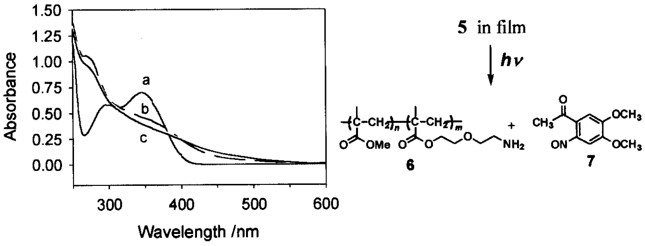
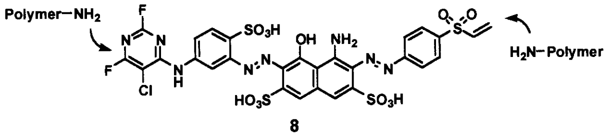


Figure 1. Time course revealed by UV absorption monitoring of a 1.5 μm thick film containing the polymer **5** on a quartz plate after irradiation with UV (360 nm) for 0 (a), 5 (b), and 20 min (c), respectively.

As displayed in Figure 1, absorption at the wavelength maximum of the protecting group decreases upon irradiation. The broad band around 400–500 nm is presumably due to the byproduct **7** from the photoreaction.



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C.I. Reactive Blue 225

Final phase of our current investigation focused on evaluation of the polymer **5** as a color imaging material. Consequently, a 1.5 mm-thick film prepared as described above on a glass substrate was irradiated with 360-nm UV for 10 min (8 mW/cm^2) through a photomask. The film was, then, incubated in a 1:1 mixture of *t*-BuOH–H_2O (aq K_2CO_3) solution containing 1 wt% of a dye **8** (C.I. Reactive Blue 225, λ_{max} = 606 nm) at room temperature for 1 h with gentle shaking. The reactive dye **8** has two electrophilic sites where free amine moieties generated upon irradiation can attack to form covalent adducts in the polymer film. It is clear from the Figure 2 that the irradiation of the film for 10 min followed by immersing the film in a dye solution affords chemisorption of the dye (Figure 2A), resulting clear color patterns on the glass substrate (Figure 2B).

In summary, we have prepared a methacrylate copolymer **5** having pendant amine precursors protected with photolabile groups. The polymer was readily spin-casted on a glass substrate and generated free amine moieties upon exposure to UV light. Incubation of the irradiated polymer film in a dye solution provided the glass substrate with color image patterns.

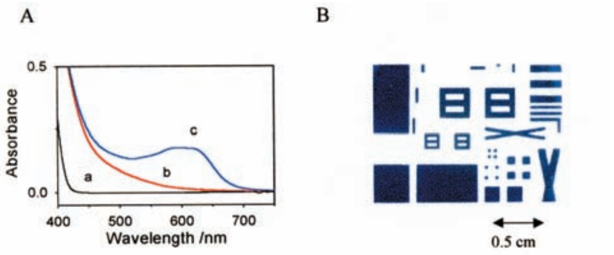

Figure 2. A: UV absorption monitoring of a 1.5 μm thick film containing the polymer **5** on a glass plate (a) before, (b) after 10 min irradiation, (c) after immersing the irradiated plate in a dye solution; B: Photograph of color patterns obtained after step (c) in A.

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References and Notes

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9 ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.60 (d, 3H), 1.96 (s, 3H), 3.34 (brt, 2H), 3.56 (brt, 2H), 3.72 (brt, 2H), 3.94 (s, 3H), 3.98 (s, 3H), 4.30 (brt, 2H), 5.38 (brs, 1H), 5.60 (s, 1H), 6.14 (s, 1H), 6.29 (q, 1H), 7.06 (s, 1H), 7.59 (s, 1H); ^{13}C NMR δ 18.1, 22.0, 40.5, 56.2, 63.4, 68.8, 69.7, 107.5, 107.7, 125.9, 134.1, 136.0, 139.6, 147.7, 153.5, 155.3, 167.3, 175.8.