

## Patterned Color Images with a Triphenylmethane-Derived Acrylate Polymer

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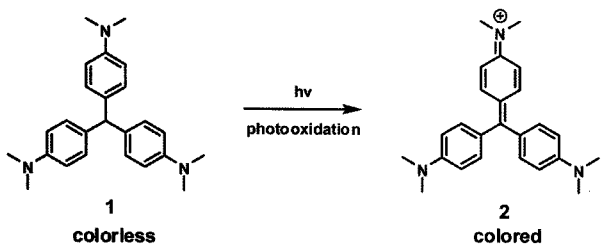
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### Introduction

Generation of patterned functional images in polymer films is of great technological importance in a variety of scientific and practical fields.<sup>1-10</sup> Among reported methods, the photoirradiation technique represents the most popular and practical approach for the patterned functional images. Typically, the photoirradiation method employs the "two-step procedure" which involves the formation of reactive species such as amines, carboxylic acids, or alcohols in the first step (photoinduced removal of protecting groups). Incubation of the polymer film in a dye solution in the second step affords the patterned functional images in the exposed areas.

We have a long-standing interest in the fabrication of patterned functional images on the solid substrates without employing the wet-developing process.<sup>11-14</sup> Accordingly, we have designed a variety of precursor molecules which undergo changes in their absorption and fluorescence properties via photoinduced structural transformations. The precursor approach allows efficient generation of patterned images in one step without the need for an additional wet process.



Scheme I. Photoinduced formation of a colored ionic material 2 from triphenylmethane derivative 1.

In general, electron-rich triphenylmethanes readily undergo photoinduced oxidation to produce colored ionic species.<sup>15</sup> For example, the colorless Leucocrystal violet 1 can be photochemically converted to the colored iminium ion 2 (Scheme I). We felt that if we could make a thin polymer film containing the colorless triphenylmethane derivative, we would be able to generate patterned color images by photoinduced selective oxidation reaction. One obvious way to make the triphenylmethane derivative more suitable for practical application is to incorporate the precursor molecule as a pendent group of a spin-castable polymer. As part of our continuing contribution to the wet-process-free patterned images, we now report a new approach for the generation of patterned color images in polymer film based on the photoinduced oxidation of triphenylmethane derivatives.

### Experimental

**Triphenylmethane Derivative 5.** *N,N*-Dimethylaniline (3) (0.36 g, 3.0 mmol), 4-nitrobenzaldehyde (4) (0.15 g, 1 mmol) and *p*-toluenesulfonic acid (0.05 g, 0.29 mmol) in benzene (0.20 mL) were stirred under a reflux condition for 6 h. The reaction mixture was diluted with benzene to twice its volume and washed twice with 10 % sodium bicarbonate solution. After concentration of the organic layer, the residue was subjected to column chromatography on silica gel (1:3 ethyl acetate : hexane) to give the intermediate 5 as a powder (0.8 g, 30%).

5: m.p. 179-180 °C; <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm) = 2.85 (s, 12H), 5.51 (s, 1H), 6.60-6.66 (d, 4H), 6.89-6.97 (d, 4H), 7.34-7.40 (d, 2H), 8.16-8.20 (d, 2H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 40.7, 54.1, 112.5, 114.9, 129.8, 130.0, 133.5, 135.6, 144.1, 148.8; IR (KBr, cm<sup>-1</sup>) 1520, 1614, 1750-1880, 2700-2950.

**Triphenylmethane Derivative 6.** To a solution of the intermediate 5 (0.54 g, 1.44 mmol) in THF (45 mL) was added 5% Pd/C catalyst (0.182 g, 1.69 mmol). The resulting mixture was stirred at room temperature for 3 h under H<sub>2</sub> atmosphere. After removal of the solid catalyst by filtration, the organic solvent was concentrated and the residue was subjected to column chromatography on silica gel (3:2 ethyl acetate : hexane) to give the intermediate 6 as a powder (0.43 g, 87%).

6: m.p. 142-144 °C; <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm) = 2.83 (s, 12H), 4.82 (s, 2H), 5.14 (s, 1H), 6.41-6.48 (d, 2H), 6.61-6.68 (d, 4H), 6.68-6.74 (d, 2H), 6.83-6.89 (d, 4H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 40.7, 54.1, 112.5, 114.9, 129.8, 130.0, 133.5, 135.6, 144.1, 148.8; IR (KBr, cm<sup>-1</sup>) 1680-1940, 2720-3010, 3300-3500.

**Acrylated Monomer TPMMA 7.** To a solution of containing 6 (0.17 g, 0.49 mmol) in 30 mL of dichloromethane was added triethylamine (0.63 mL, 4.49 mmol) and methac-

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royl chloride (0.05 g, 0.45 mmol). The resulting mixture was stirred at room temperature for 12 h under nitrogen atmosphere. After concentration in vacuo, the residue was subjected to column chromatography on silica gel (1:2 ethyl acetate: hexane) to give the intermediate **7** as a powder (0.133 g, 65%).

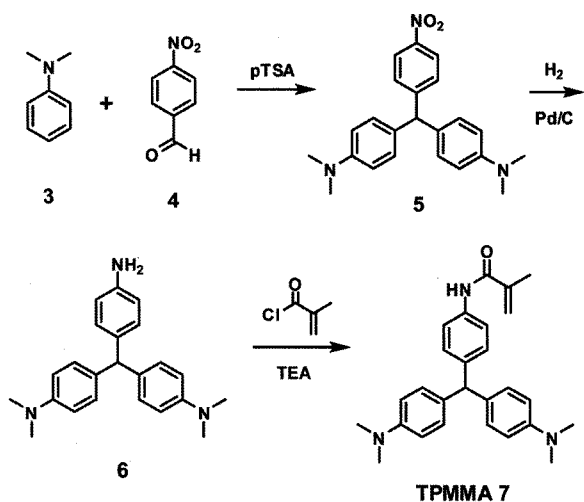
**7**: m.p. 175–176 °C;  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ ),  $\delta$  (ppm) = 1.97 (s, 3H), 2.84 (s, 12H), 5.24 (s, 1H), 5.48 (s, 1H), 5.76 (s, 1H), 6.61–6.68 (d, 4H), 6.82–6.89 (d, 4H), 6.94–7.02 (d, 2H), 7.56–7.61 (d, 2H), 9.74 (s, 1H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm) = 19.0, 41.0, 54.7, 112.8, 119.9, 120.1, 130.1, 130.2, 133.0, 135.8, 141.2, 142.0, 149.2, 166.8; IR (KBr,  $\text{cm}^{-1}$ ) 1520, 1616, 1820–1930, 2750–2960, 3150–3370.

**Copolymer P(TPMMA/MMA) 8**. A solution containing monomer **7** (0.25 g, 0.60 mmol), MMA (0.30 g, 3.0 mmol), AIBN (0.006 g, 0.037 mmol) and DMF (2 mL) in an ampoule was subjected to repeated freeze-thaw cycles before the ampoule was sealed under vacuum. The sealed ampoule was heated at 70 °C for 18 h. After polymerization, the product was diluted with tenfold THF, precipitated into excess hexane, and washed with methanol. Polymers were filtered off and dried to give 0.385 g of P(TPMMA/MMA) as a pale green powder.

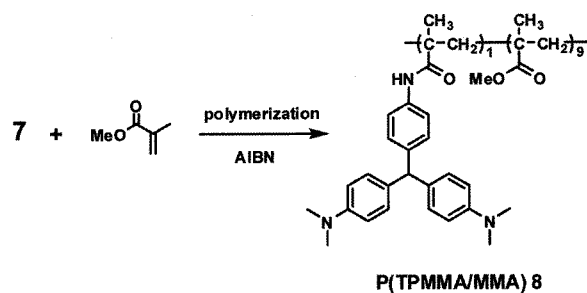
## Results and Discussion

The strategies employed for the synthesis of triphenylmethane-derived monomer **7** is shown in Scheme II. Condensation of *N,N*-dimethylaniline (**3**) and 4-nitrobenzaldehyde (**4**) in the presence of *p*-toluenesulfonic acid (PTSA) afforded triphenylmethane derivative **5**. Hydrogenation of **5** followed by coupling of the intermediate **6** with methacryloyl chloride provided the desired acrylate monomer TPMMA **7** in a moderate yield (65%).

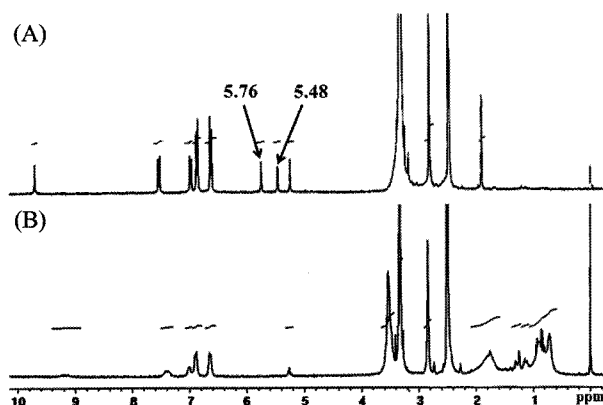
Copolymerization of the triphenylmethane-derived acrylate monomer **7** with methyl methacrylate (MMA) was carried out with a 1: 5 molar feed ratio in DMF using 2,2'-azobis



**Scheme II.** Synthesis of triphenylmethane-derived monomer **7**.



**Scheme III.** Preparation of polymer **8** containing triphenylmethane moieties.

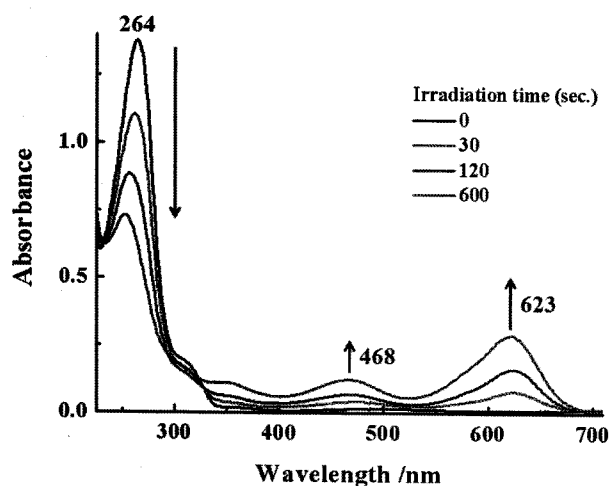


**Figure 1.**  $^1\text{H-NMR}$  spectra of triphenylmethane-containing monomer TPMMA **7** (A) and the copolymer P(TPMMA/MMA) **8** (B).

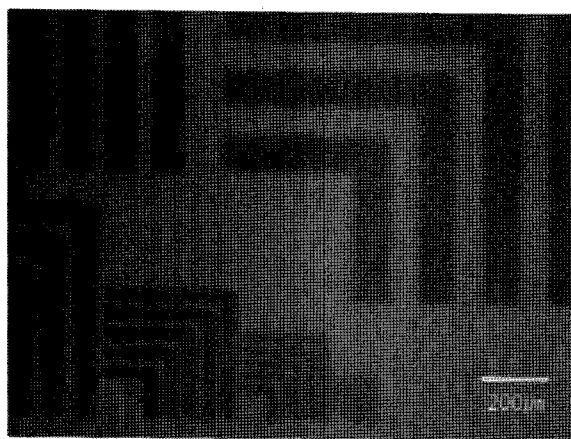
(isobutyronitrile) (AIBN) as a radical initiator (Scheme III). The copolymer, P(TPMMA/MMA) **8**, after precipitation in hexane, was obtained in 50% yield. The polymer has a weight-average molecular weight ( $M_w$ ) of 7,300 with a polydispersity of 1.81. The 1:9 ratio of triphenylmethane monomer to MMA in polymer **8** was confirmed by  $^1\text{H-NMR}$  analysis.

Figure 1 displayed  $^1\text{H-NMR}$  spectra of the acrylate monomer TPMMA **7** and the copolymer P(TPMMA/MMA) **8**. It can be clearly seen from the spectra that polymerization results in the disappearance of vinyl protons at 5.47 and 5.78 ppm.

In order to investigate the feasibility of photoinduced colored iminium ion formation, a thin polymer film (ca. 1  $\mu\text{m}$  thickness) of the copolymer **8** was prepared by spin-coating a chloroform solution on a quartz plate. The film was irradiated with UV light (254 nm, 1  $\text{mW}/\text{cm}^2$ ) and the progress was monitored by UV/Vis spectroscopy. As displayed in Figure 2, absorption at the wavelength maximum of the triphenylmethane chromophore (264 nm) decreases upon irradiation and new absorption peaks in the visible absorption region (468 and 623 nm) appear. The generation of absorption peaks in the visible region is ascribed to the formation of iminium ion species and is further evidenced by comparison of the color of the film before and after irradiation.



**Figure 2.** UV-visible spectroscopic monitoring of the thin polymer film derived from the copolymer **8** upon 254 nm UV irradiation.



**Figure 3.** Color image patterns obtained by photomasked UV irradiation (254 nm, 1 mW/cm<sup>2</sup>, 5 min) of a ca. 1 mm thick polymer film prepared with the copolymer **8**.

tion. When the colorless and transparent film was exposed to UV light, a highly transparent green colored film was obtained.

Final phase of current investigation focused on the evaluation of the copolymer **8** as a latent color imaging material. Consequently, a spin-coated ca. 1  $\mu\text{m}$  thick film obtained with the copolymer **8** was irradiated with 254 nm UV light for 5 min through a photomask. The photograph shown in Figure 3 reveals green image patterns under an optical microscope. The green colored areas are the portions exposed through the photomask.

## Conclusions

In summary, we have prepared a precursor polymer containing pendent triphenylmethane moieties for patterned color images. The triphenylmethane groups in polymer **8** were found to undergo photoinduced oxidation to produce colored iminium ion species in the polymer film. When the polymer film was exposed to UV light through a photomask, well-resolved color image patterns were readily obtained without any further wet development. The simple and straightforward strategy described above should be an additional significant contribution to the technology aimed for the wet-process free patterned color image.

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