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Photoacid-Induced Fluorescence Quenching: A New Strategy for Fluorescent Imaging in Polymer Films**

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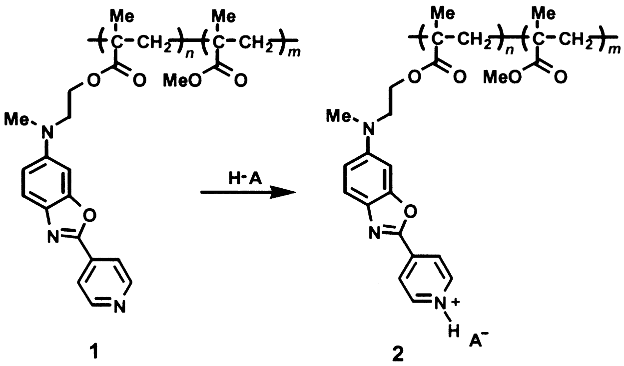
The generation of patterned images in polymer films has gained much attention in fundamental and applied research areas. The development of patterned functional images is also of great importance in the electronics industry. Recently, the generation of functional images by selective immobilization of organic dyes in polymer films has been reported.[1–3] The selective removal of labile acidic protecting groups by photo-induced chemical transformation followed by chemisorption of organic dyes from solution into the patterned polymer film afforded μm-scale functional images. Recently, we described finely resolved patterned fluorescent images with these transiently protected precursor molecules.[4, 5] As part of our efforts to produce functional images in polymer films we now report the synthesis of the novel copolymer **1**, which has pendant pyridylbenzoxazole groups, and its use in the generation of fluorescent images by photolithographic methods.



1 **2**

The strategy for the design of a molecule for fluorescent imaging is based on the following facts: in a conjugated aromatic system, the nature of fluorescence is often greatly affected by substituents. A strong fluorescence is, in general, observed when an aromatic compound has extended π conjugation and contains electron-donor substituents, such as hydroxy or amino groups, at both ends of this conjugated system. The fluorescence of the molecule, however, drastically decreases if one of the electron-donating substituents is replaced by an electron-withdrawing substituent, such as a nitro group. An electron-withdrawing effect, leading to fluorescence quenching, can also be induced when the fluorescent chromophore has a functional group which can interact with an acid. We have now designed the copolymer **1**, which has fluorescent pyridylbenzoxazole moieties as pendant groups. The benzoxazole chromophore of **1** has an electron-donating amino group at one end and an electron-rich pyridyl group at the other. However, the strongly fluorescent nature of **1** is expected to be affected when the electronic state of the benzoxazole chromophore is disturbed by interaction with an acid, as in **2**. If the acid-induced fluorescence quenching is significant, and occurs only in selected areas, then patterned fluorescent images will be obtained.

The preparation of the pyridylbenzoxazole monomer **8** is shown in Scheme 1. In general, benzoxazole derivatives are prepared by a prior formation of an *o*-hydroxy amide through the condensation of *o*-aminophenol with an acid chloride at low temperature, followed by thermal cycloaddition at high temperature.[6] In this cyclization step unwanted side reactions often occur. To avoid these we have developed a reaction with mild conditions for the formation of the benzoxazole ring. Thus, protection of the hydroxy group of 5-fluoro-2-nitrophenol (**3**) followed by aromatic substitution with (2-methylamino)ethanol provided the alcohol **5** in good yield, which was converted to pyridylbenzoxazole **7** in three steps. The removal of the protecting group and reduction of the nitro group by hydrogenation followed by treatment with 4-pyridinecarboxaldehyde gave the imine intermediate **6**. The oxidative cyclization of **6** with lead(IV) acetate, at room temperature, provided the benzoxazole chromophore **7** in high yield (80% from **5**). Purification after the deprotection, imine formation, and cyclization steps was not necessary. The pyridylbenzoxazole **7** was converted into the desired monomer **8** (4PBZMA) by treatment with methacryloyl chloride.

Copolymerization of the monomer **8** with methyl methacrylate (MMA) was carried out with a 1:1 molar feed ratio in

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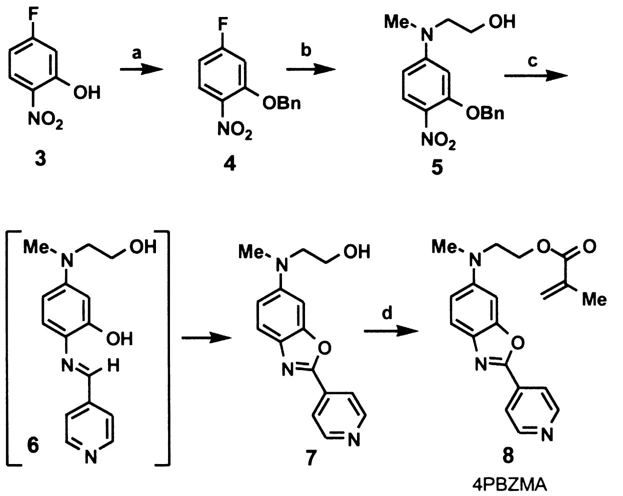

Scheme 1. Synthesis of the pyridylbenzoxazole monomer **8**. a) Benzyl bromide, K_2CO_3, DMF, 100 °C, 3 h, 83 %; b) 2-(methylamino)ethanol, K_2CO_3, DMF, 100 °C, 3 h, 85 %; c) 1. H_2, 10 % Pd/C, THF, 25 °C, 12 h; 2. 4-pyridinecarboxaldehyde, THF, 25 °C, 3 h; 3. $Pb(OAc)_4$, THF, 25 °C, 3 h, 80 % from **5**; d) methacryloyl chloride, TEA (triethylamine), CH_2Cl_2, 25 °C, 12 h, 74 %.

1-methyl-2-pyrrolidinone (NMP) using 2,2′-azobis(isobutyronitrile) (AIBN) as a radical initiator. The copolymer **1**, after precipitation into methanol, was obtained as a yellow powder in 59 % yield. The polymer has a weight-average molecular weight (M_w) of 61 000 with a polydispersity of 2.07. The 4:6 ratio of pyridylbenzoxazole monomer to MMA in **1** was confirmed by NMR and UV spectroscopic analyses.

The UV/Vis spectrum of **1** has a maximum absorption wavelength at 378 nm which is attributed to the pyridylbenzoxazole groups. To investigate the possible formation of **2** and the fluorescence quenching by acid-induced chemical transformation, a thin polymer film containing **1** (77 wt %) and a photoacid generator (triphenylsulfonium hexafluoroantimonate (TPSHFA),[7–10] 23 wt %) was prepared by spin-coating a chloroform solution on a quartz plate. This film was irradiated with UV light (360 nm) and the progress was monitored by both UV/Vis and fluorescence spectroscopy. As displayed in Figure 1 a, absorption at the wavelength maximum of the benzoxazole chromophore (378 nm) decreased upon irradiation and a new band appeared at 486 nm. The position of this new wavelength maximum (486 nm) is in the region expected for the protonated benzoxazole chromophore found in **2**. The formation of the protonated species **2** in the polymer film was also deduced from comparison of the color of the film before and after irradiation. When the lightly yellow, transparent polymer film was exposed to UV light for 30 s, a highly transparent red film was obtained. These results demonstrate that the strong acid (presumably hydrogen fluoride (HF) and/or hydrogen hexafluoroantimonate ($HSbF_6$)), generated by irradiation of the photoacid generator, protonates the nitrogen atoms of the pyridyl groups. The two isosbestic points (331, 422 nm) demonstrate that the process is an A- to B-type conversion without intermediate species. More interesting results became apparent from a comparison of the fluorescence spectra before and after irradiation. Irradiation of the polymer film for 10 s resulted in the disappearance of the fluorescence at 600 nm (Figure 1 b). Further irradiation had no substantial effect on the fluorescence quenching.

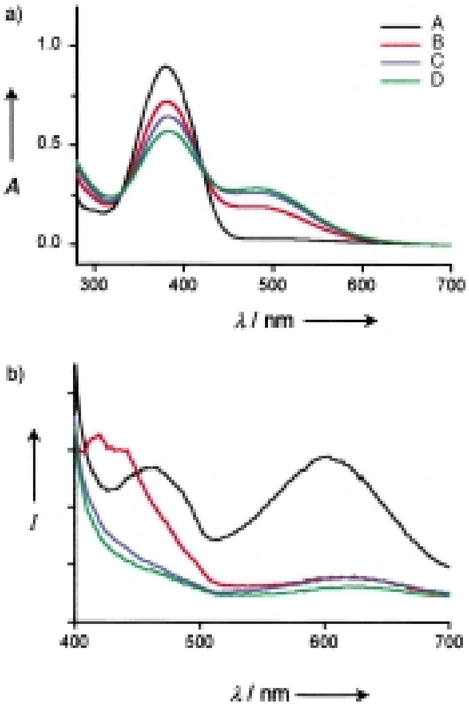

Figure 1. Time course revealed by a) UV absorption and b) fluorescence emission spectroscopy. Monitoring of a 0.2-μm thick film containing polymer **1** (77 wt %) and the photoacid generator TPSHFA (23 wt %) on a quartz plate after UV irradiation (360 nm) followed by heating at 120 °C for 1 min (irradiation time: (A) 0, (B) 10, (C) 30, (D) 180 s, respectively).

Formation of patterned fluorescent images with **1** requires generation of acids in the specific areas. For this purpose, a polymer film containing **1** and TPSHFA on a silicon wafer was exposed through a photomask. As shown in Figure 2, fluorescent image patterns appeared under fluorescent microscopy, the dark areas are the portions exposed through the photomask.

We have prepared a polymer having pyridylbenzoxazole pendants for fluorescent imaging. Synthesis of the monomer was straightforward and the copolymer **1** was readily prepared from an AIBN-initiated radical polymerization with methyl

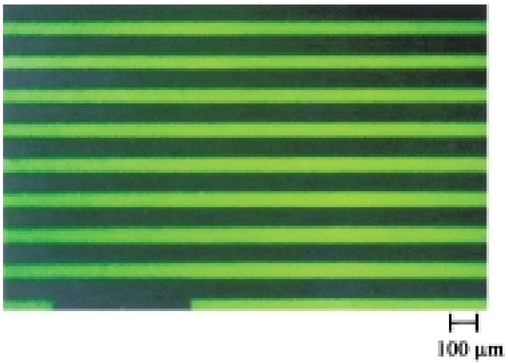

Figure 2. Fluorescent image patterns obtained with a 1.0-μm thick film containing copolymer **1** (77 wt %) and TPSHFA (23 wt %) on a silicon wafer after UV irradiation (360 nm) for 10 s (200 mJ cm^{-2}) through a photomask followed by heating at 120 °C for 1 min.

methacrylate as a comonomer. The copolymer **1** was shown to have good film-forming properties on a solid substrate. The fluorescence of the polymer was effectively quenched by photochemically generated acid and afforded finely resolved fluorescent images on a solid substrate.

Experimental Section

4: Potassium carbonate (82.9 g, 0.60 mol) and benzyl bromide (136.8 g, 0.80 mol) were added to a solution of 5-fluoro-2-nitrophenol (**3**) (94.3 g, 0.60 mol) in DMF (200 mL). The resulting mixture was stirred at 100 °C for 3 h, filtered, and the filtrate diluted with diethyl ether. The organic layer was washed with water and dried with anhydrous magnesium sulfate. Concentration, followed by vacuum distillation (142–146 °C, 0.1 Torr) of the residue gave **4** (123.1 g, 83 %) as a yellow solid. M.p. 55–56 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.18$ (s, 2H), 6.66–6.87 (m, 2H), 7.32–7.49 (m, 5H), 7.94 (d, 1H); elemental analysis calcd (%) for $C_{13}H_{10}N_1O_3F_1$ (247.23): C 63.16, H 4.08, N 5.67; found: C 63.50, H 4.09, N 5.21.

5: Potassium carbonate (51.83 g, 0.38 mol) was added to a solution of **4** (123.1 g, 0.50 mol) and 2-(methylamino)ethanol (56.3 g, 0.75 mol) in DMF (200 mL). The resulting mixture was heated at 100 °C for 3 h and poured into water (1 L). The yellow precipitate was collected, dried, and dissolved in THF. Precipitation into hexane provided **5** (128.4 g, 85.3 %). M.p. 104–106 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.41$ (s, 1H), 3.03 (s, 3H), 3.50 (t, 2H), 3.77 (t, 2H), 5.13 (s, 2H), 6.10–6.22 (m, 2H), 7.27–7.50 (m, 5H), 7.88 (d, 1H); elemental analysis calcd (%) for $C_{16}H_{18}N_2O_4$: (302.33): C 63.57, H 6.00, N 9.27; found: C 63.50, H 6.09, N 9.21.

7: A mixture of **5** (24.2 g, 0.08 mol) and 10 % Pd/C (3.9 g) in THF (200 mL) was stirred under hydrogen at 25 °C for 12 h. The catalyst was removed by filtration, and 4-pyridinecarboxaldehyde (8.57 g, 0.08 mmol) was added to the filtrate. The resulting solution was stirred at 25 °C for 3 h. Lead(IV) acetate (44.38 g, 0.10 mol) was slowly added to the solution and the mixture stirred vigorously at 25 °C for 3 h. Removal of lead diacetate followed by flash column chromatography (silica gel, THF) gave **7** (17.14 g, 80.0 %) as a yellow solid. M.p. 178–180 °C; ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 3.03$ (s, 3H), 3.34–3.63 (m, 4H), 4.72 (t, 1H), 6.88 (d, 1H), 7.01(s, 1H), 7.51 (d, 1H), 7.97 (d, 2H), 8.78 (d, 2H); elemental analysis calcd (%) for $C_{15}H_{15}N_3O_2$ (269.30): C 66.9, H 5.61, N 15.60; found: C 66.1, H 5.69, N 15.41.

8: The benzoxazole intermediate **7** (4.80 g, 17.84 mmol) was dissolved in dichloromethane (200 mL) and methacryloyl chloride (3.73 g, 35.68 mmol) and TEA (6.0 mL, 43.11 mmol) were added. The mixture was stirred at 25 °C for 12 h, poured into water, and extracted with dichloromethane. The organic layer was concentrated in vacuo, and silica gel column chromatography (25 % EtOAC/hexane) afforded **8** (4.47 g, 74.4 %). M.p. 60–62 °C; λ_{max} ($CHCl_3$) = 378 nm; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.90$ (s, 3H), 3.07 (s, 3H), 3.73 (t, 2H), 4.36 (t, 2H), 5.53 (s, 1H), 6.05 (s, 1H), 6.82–6.87 (m, 2H), 7.60 (d, 1H), 7.99 (d, 2H) 8.74 (d, 2H); elemental analysis calcd (%) for $C_{19}H_{19}N_3O_3$ (327.38): C 67.64, H 5.68, N 12.45; found: C 67.9, H 5.74, N 12.2.

Copolymer 1 P(4PBZMA/MMA): A solution containing monomer **8** (0.50 g, 1.48 mmol), MMA (0.15 g, 1.49 mmol), AIBN (9.7 mg) and NMP (2.5 mL) in an ampoule was subjected to repeated freeze–thaw cycles before the ampoule was sealed under vacuum. The sealed ampoule was heated at 65 °C for 40 h. After polymerization, the product was precipitated into methanol and dried to give **1** (0.385 g, 59.2 %) as a yellow powder.

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Halogen Bonding versus Hydrogen Bonding in Driving Self-Assembly Processes[**]

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It is well known[1] that carbon-bound halogen atoms (frequently iodine and bromine, but also chlorine and even fluorine) can act as electron acceptors and form short contacts with different species (both neutral and negatively charged) that possess an ability to act as an electron donor.[2] These noncovalent interactions can be strong enough to control the aggregation of organic molecules in solid,[3] liquid,[4] and gas[5, 6] phases and the term "halogen bonding"[2, 6] has been suggested in order to emphasize the similarity with hydrogen bonding. While metal-ion coordination[7] is frequently the key feature in inorganic supramolecular systems, hydrogen bonding[8] is by far the most frequently used tool to assemble organic molecules in solid, liquid, or gas phases, and it plays an important role in stabilizing supramolecular aggregates even in water.

Here we show that when the recognition pattern controlling the self-assembly process can be based on either hydrogen or halogen bonding, the latter can dominate over the former and, under appropriate conditions, will single out the molecules that will be involved in the construction of supramolecular architectures. We have already described specific I⋯N intermolecular interactions occurring between α,ω-diiodoperfluoroalkanes and dinitrogen hydrocarbons.[9–11] These interactions are strong enough to overcome the low affinity[12] that exists between perfluorocarbons and hydrocarbons to assemble them into oligomeric structures in the liquid phase[4] and into crystalline 1D networks in the solid phase.[9–11]

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