

# Chemically amplified photolithography of a conjugated polymer

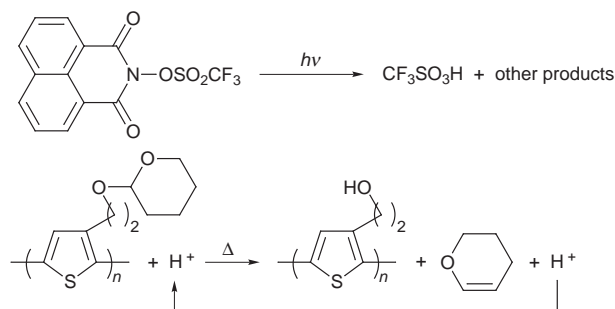
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The solid state photocatalytic reaction between trifluoromethanesulfonic acid and poly{3-[2-(tetrahydropyran-2-yloxy)ethyl]thiophene} is employed to fabricate polymeric patterns of conjugated polymer.

Microelectronic technologies routinely image polymer films using photolithography. Similar techniques have been employed to deposit conjugated polymers because of their attractive microelectronic and optoelectronic properties.<sup>1</sup> Here we describe a strategy which enhances the photoreactivity of conjugated polymers and facilitates their photolithography. The concept uses chemical amplification which was first demonstrated in photolithography with polystyrene based polymers.<sup>2</sup> The first example of chemical amplification in the photolithography of a conjugated polymer is demonstrated below (Scheme 1) for a polythiophene derivative possessing pendant THP functionality in the presence of a photoacid generator (PAG).

Poly{3-[2-(tetrahydropyran-2-yloxy)ethyl]thiophene} (PTHPET) was synthesized by the following procedure. 2-(3-Thienyl)ethanol was brominated selectively with 1 equiv. of NBS in DMF, and was protected by reacting with 5 equiv. of dihydropyran to afford 2-bromo-3-[2-(tetrahydropyran-2-yloxy)ethyl]thiophene.<sup>3</sup> The regioregular polymer PTHPET was prepared by cross-coupling of the corresponding 5-Grignard reagent.<sup>4</sup> The polymer was precipitated and purified from MeOH. The structure of the polymer was confirmed by NMR spectroscopy: resonance peaks in the <sup>1</sup>H NMR spectra centered at 7.12, 4.56 and 3.09 ppm were assigned to the thienyl ring, the methine of the THP moiety, and the  $\alpha$ -methylene, respectively.<sup>3a</sup> Eleven resonance peaks were observed in the <sup>13</sup>C NMR spectra. Four peaks at 129.5, 132.0, 133.7 and 136.5 ppm were assigned to thienyl ring carbons.<sup>4</sup> The observed peaks at 98.8, 19.5, 25.6, 30.7 and 62.1 ppm are characteristic of the THP group.<sup>5</sup> Peaks at 30.0 and 67.1 ppm were assigned to  $\alpha$ - and  $\beta$ -methylene carbons, respectively. The regioregularity of the polymer is evidenced by the fact that only four aromatic carbon signals and only one  $\alpha$ -methylene carbon signal were observed. Molecular weight and molecular weight distribution were measured by GPC in THF solution and calibrated against poly(3-hexylthiophene) standards:<sup>6</sup>  $M_w = 1.15 \times 10^4$ ,  $M_w/M_n = 1.73$ . The photoacid generator, *N*-(trifluoromethylsulfonyloxy)-1,8-naphthalimide, was a gift from the IBM Research Division, San Jose, CA.



Scheme 1 Reaction scheme for chemically amplified photolithography of PTHPET

PTHPET is thermally stable up to  $\sim 220$  °C whereupon a 30% weight loss was observed between 220 and 275 °C by TGA. The weight loss is consistent with the deprotection scheme shown in Scheme 1 in the absence of a catalytic proton. When mixed with trifluoromethanesulfonic (triflic) acid (5 mol% based on the thienyl unit), films of PTHPET are chemically stable at room temperature. However, upon heating, the deprotection temperature for the polymer was lowered to 120 °C. Furthermore, deprotection is complete indicating that the reaction is catalyzed by the presence of acid.

Upon thermolysis of PTHPET in the presence of triflic acid, FTIR showed the emergence of a broad signal at  $\sim 3400$   $\text{cm}^{-1}$  due to  $-\text{OH}$ . This occurred concomitantly with the deprotection temperatures determined by TGA. There was also a significant decrease in the signals due to the THP group. Cleavage of THP from PTHPET gave rise to dramatic changes in the absorption spectra. PTHPET alone yielded classical reversible thermochromism between 20 and 210 °C (Fig. 1) but in the presence of 5 mol% triflic acid,  $\lambda_{\text{max}}$  dramatically increased at 130 °C upon heating. The red-shift is explained by the sudden release of steric hindrance caused upon elimination of the bulky THP group. The absorption spectra and  $\lambda_{\text{max}}$  became independent of temperature upon further heating or subsequent cooling cycles which is consistent with the increase in compactness associated with the shorter side-chain polymer and/or the existence of strong hydrogen bonding between ethanolic side-chains.

PTHPET is completely soluble in common organic solvents, whereas the resultant polymer following cleavage is not. This is the result of a significant change in the length and polarity of the side-chain. This observation, in conjunction with the acid-catalyzed nature of the deprotection process, gave the impetus to examine chemically amplified photolithography of PTHPET in the presence of a photoacid generator (Scheme 1). Films of PTHPET containing 20 mol% of the PAG were cast from THF solution. The PAG exhibited a broad absorption spectrum,  $\lambda_{\text{max}}$  336 nm, and generates triflic acid when irradiated. Films were irradiated with UV-VIS light from a 1000 W Xe lamp through a 361 nm broadband filter with an irradiation intensity of 0.18  $\text{mW cm}^{-2}$ . The temperature dependant absorption spectra of

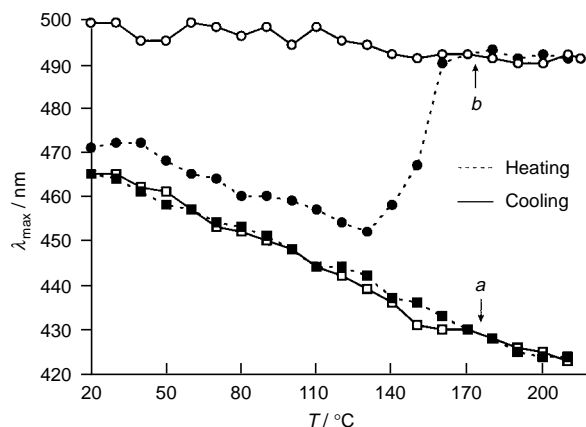
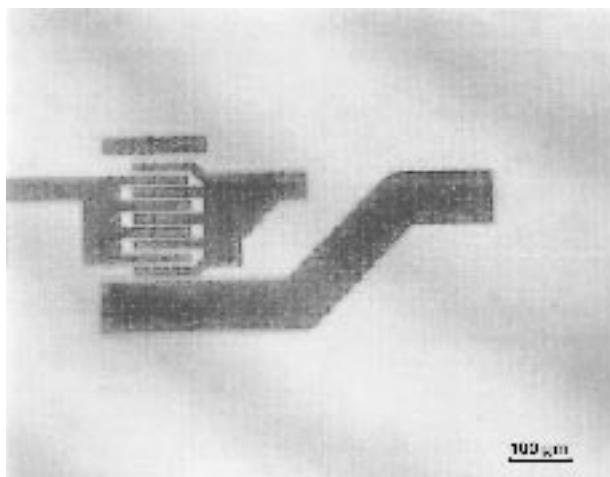


Fig. 1 Temperature dependence of  $\lambda_{\text{max}}$  for films of PTHPET (a) in the absence, and (b) presence of 5 mol% triflic acid



**Fig. 2** Micrograph of conjugated polymer obtained by chemically amplified photolithography

photolyzed composite films was recorded following irradiation and showed a dramatic red-shift  $\lambda_{\max}$  at 120 °C, *i.e.* similar to that observed for films containing triflic acid (Fig. 1). This is strong evidence for the catalytic cleavage of THP initiated through photogeneration of triflic acid. FTIR confirmed the reaction and the resultant photolyzed films were insoluble in common organic solvents.

Chemically amplified photolithography was demonstrated by irradiating similar composite films (~300 nm thick) through a photomask. The films were subsequently heated to 125 °C for 2.5 min and developed with THF, whereupon only the unexposed polymer dissolved. A patterned image of the conjugated polymer is presented in Fig. 2. The resolution of the smallest features is 15  $\mu\text{m}$  and is limited by the optical apparatus. Due to the catalytic nature of this reaction relatively low irradiation doses were required for imaging (65  $\text{mJ cm}^{-2}$ ). Thus, the degree of photobleaching of the polymer was negligible. Conductivity measurements on the photochemically deprotected polymer doped with a variety of oxidants yielded conductivities very similar (1–4  $\text{S cm}^{-1}$ ) to the triflic acid

deprotected polymer, confirming that  $\pi$ -conjugation was retained.

Spectroscopic, thermogravimetric, solubility and microscopic analyses confirm the reaction presented in Scheme 1. The reaction does not proceed in the solid state at room temperature at an appreciable rate. Upon heating, the reaction rate is increased either through an increase in free volume of the polymer and/or an increase in the rate constant. This is a favourable observation since it infers that the spatial extent of the imaging chemistry can be controlled following irradiation. Studies are underway to determine the electronic, optical and photonic properties of micron-sized polymeric patterns fabricated using this and similar chemical schemes.

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## Notes and References

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