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Direct Thermal Patterning of a π-Conjugated Polymer

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A method for the direct thermal patterning of a thermally labile π-conjugated polymer film containing a NIR sensitive dye using a continuous wave 830 nm NIR diode laser is described. The method is demonstrated with poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) (PTHPET), which is rendered insoluble upon localized heating with the NIR irradiation due to catalytically enhanced elimination and volatilization of dihydropyran. The optical and photophysical properties of the patterned π-conjugated material are described. High-resolution pixels (10 μm) of conjugated polymer can be obtained with laser dosages as low as 600 mJ/cm^2 at laser scan speeds of 0.6 m/s. The method is capable of imaging large surface areas, up to 1 m^2, at relatively high throughput and with micrometer size resolution, and thus could find application where the patterning of electroluminescent and/or conducting organic materials are required.

Introduction

The advancement of high-performance display technology is central to the growth of information technology, particularly in the electronic device sector. The next generation of displays must be thinner, more energy efficient, full color, high resolution, and less expensive. In this regard many research organizations are paying close attention to developments of "π-conjugated polymers", πCPs, and are aggressively pursuing research programs aimed at speeding up their implementation. πCPs possess a number of important electronic properties that make them interesting. In the neutral form they are semiconductors and their conductivity can be reversibly modulated by application of an electric field, which makes them attractive candidates as active materials in organic field effect transistors (OFETs).[1−3] Many πCPs are highly luminescent and are sought after as active materials in electroluminescent devices. In the oxidatively doped form, they are electronically conductive, thus potentially serving as conductive films, transparent conductive coatings, or interconnects in novel electronic circuitry.

Organic semiconductors are different from conventional inorganic semiconductors: processing is simpler, e.g., spin coating, evaporation, or printing;[4−6] there is good compatibility with substrates including flexible plastics; and there are excellent opportunities for structural diversity. Nevertheless, there are drawbacks. In the case of OFETs there is a need to improve charge mobility and reliability; in organic light emitting devices (OLEDs) the quest is for stable, highly electroluminescent materials with tunable emission; in electronic interconnects, higher stability of the oxidatively doped state is required. Rapid advances are being made in the development of materials particularly for OFETs and OLEDs with the expectation that wide commercial application of these devices may soon be realized. A critical, common concern in this technology, however, is device fabrication, requiring reproducible deposition of active material with micrometer (10−100 μm) resolution.

Techniques for patterning πCPs generally fall into the reactive and the nonreactive. The former include area-selected electropolymerization on patterned self-assembled monolayers, direct writing using electrochemical scanning probe microscopy, or photochemical patterning such as photolithography, photoablation, and photobleaching, which are based on the specific reactivity of a particular conjugated system. Nonreactive patterning methods include screen printing, soft lithography, and ink-jet printing. The latter are generic techniques that make use of preformed polymers and do not rely on a material's reactivity.

Photolithography of πCPs differs from conventional lithography. In the latter there is usually no consideration of the intrinsic electronic property of the polymer resist because it usually plays no active role in device operation; in contrast, πCPs must retain their electronic and optical properties in order for them to function as intended. Since photolithography often involves direct irradiation of the conjugated polymer, the material's photochemistry plays a pivotal role. Several reviews on the subject exist, and many different classes of polymers have been studied.[7,8] These include

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(1) Dimirakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.

(2) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359.

(3) Abdou, A.; Lu, X.; Xie, Z. W.; Orfino, F.; Deen, M. J.; Holdcroft, S. *Chem. Mater.* **1995**, *7*, 631.

(4) Hebner, T. R.; Wu, C. C.; Mercy, M. H.; Lu, H.; Sturm, J. C. *Appl. Phys. Lett.* **1998**, *72*, 519.

(5) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, Y.; Yang, Y. *Nat. Mater.* **2005**, 1.

(6) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* **2000**, *290*, 2123.

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polyacetylene, *trans*-1,4-polybutadiene, poly(*p*-phenylene sulfide), poly(*p*-phenylene vinylene), polyanilines, and polythiophenes. However, it has been shown that direct photopatterning more often than not leads to photo-oxidation of the polymer.[9] Photo-oxidation, however slight, has a deleterious effect on its properties, in particular, electroluminescence. πCPs have thus been designed to be more photosensitive, from the perspective of patterning, by attaching labile moieties to the main chain.[10] A drawback, however, is that πCPs are highly absorbing in the UV−vis region: a property that limits imaging to thin films.

It may be that photochemical patterning is too complex and too expensive in the short term for mass fabrication of polymer-based electronics and that a more desirable patterning methodology is needed that is technically simpler and more versatile. Indeed, many πCPs are aptly suited for simpler patterning techniques, such as screen printing, by virtue of their solubility. Thus, reports of all-polymer field effect transistors fabricated by printing techniques have generated considerable interest.[1,11,12] The current drawback of screen printing, however, appears to be lack of resolution and reproducibility. The desirable <10 μm resolution preferred for many devices is not easily achievable. Furthermore, since many conjugated polymers are not highly soluble, their solution viscosity may be too low. In a novel variation, microcontact printing (μCP)[13,14] has been used to deposit a soluble poly(3,4-ethylenedioxythiophene)−polystyrene sulfonate conducting polymer complex (PEDOT-PSS) directly onto ITO and gold electrodes to yield conducting polymer lines with 100 μm features.[15] Another promising technique, ink-jet printing, relies on the steering of material-containing droplets discharged from a nozzle and their contained impact and solidification onto substrates. The impinging droplet must rapidly wet the substrate, bind, and evaporate, before lateral displacement occurs.[4,6] To restrict the spreading of droplets upon impact, and thus achieve higher resolution, substrates have been selectively patterned so as to possess hydrophobic and hydrophilic surface regions.

A variety of techniques are available for patterning π-conjugated polymers. The technique of choice depends on the material under consideration, the substrate, and the intended application. Both photolithographic and nonreactive techniques may be appropriate, although much has been speculated on the unique opportunity to pattern conjugated materials at low cost using the latter by virtue of the fact that solutions of the active material can be prepared. Pattern resolution generally increases on going from screen printing, to ink-jet printing, to soft lithographic techniques. All three techniques may or may not be acceptable in the very near future in patterning mass-produced components for light-emitting devices, for example. Furthermore, it can be argued that it is unlikely that nonreactive techniques can compete with photolithographic techniques in terms of resolution or reproducibility; hence, despite the apparent simplicity of printing techniques, photopatterning techniques should not be dismissed where the patterning of πCPs is concerned.

Notably, the technique used to mass-produce sub-10 μm pixels of organic material is found in the graphic arts industry and uses the concept of direct thermal imaging. The fundamental concepts behind thermal patterning are well-documented[16,17] and have been perfected by several companies. Currently, it involves the delivery of near-infrared (NIR) light pulses from an inorganic diode laser onto a polymer film containing a NIR-absorbing dye. Typically, the polymer does not absorb the irradiation but the dye, upon doing so, converts the NIR photons into heat by internal conversion.[18,19] The temperature of the irradiated regions rises rapidly over a period of microseconds, which initiates a highly localized chemical or physical change in the polymer. The local spot temperature can be controlled up to several hundreds of degrees by control of the incident power and absorption cross section. Sophisticated optics deliver hundreds of NIR laser beams simultaneously so that large formats may be scanned very rapidly. The resolution of the image is typically 5−10 μm, and even smaller with more sophisticated equipment. In current lithographic printing technology, printing plates are composed of a thin layer of thermal or photosensitive hydrophobic polymer film and a hydrophilic substrate. The solubility of the polymer films changes in a region where the NIR pulse strikes and can be dissolved in a developing solution. The finished plate bears a hydrophobic image on a hydrophilic substrate. When ink is applied, it adheres to the hydrophobic image. Transfer of the ink to paper or another suitable medium results in an image of photographic resolution. A type of thermal patterning of a πCP has already been reported wherein an organic donor film and acceptor substrate are brought into physical contact and a laser beam is directed at the backside of the donor film so as to propel the organic material toward the acceptor substrate.[20] After laser exposure is complete, the donor layer is removed, leaving a negative-tone pattern of organic material.

In a previous report describing the photolithography of polythiophene derivatives we reported that tetrahydropyranyl (THP) functionality attached to polythiophene can be catalytically cleaved by acid in the solid state with close to 100% efficiency according to the reaction scheme below.[21] The polymer, poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) (PTHPET), is thermally stable up to ∼220 °C whereupon a

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(7) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 1.

(8) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(9) Kocher, C.; Montali, A.; Smith, P.; Weder, C. *Adv. Funct. Mater.* **2001**, *11*, 31.

(10) Yu, J.; Abley, M.; Yang, C.; Holdcroft, S. *Chem. Commun.* **1998**, 1503.

(11) Choi, W. M.; Park, O. O. *Microelectron. Eng.* **2004**, *73*, 178.

(12) Xu, G.; Bao, Z.; Groves, T. *Langmuir* **2000**, *16*, 1834.

(13) Yu, J.; Holdcroft, S. *Chem. Mater.* **2002**, *14*, 3705.

(14) Pisignano, D.; Persano, L.; Cingolani, R.; Gigli, G.; Babudri, F.; Farinola, G. M.; Naso, F. *Appl. Phys. Lett.* **2004**, *84*, 1365.

(15) Granlund, T.; Nyberg, T.; Roman, L. S.; Svensson, M.; Inganas, O. *Adv. Mater.* **2000**, *12*, 269.

(16) Baetzold, J.; Bellmann, E.; Savvateev, V.; Wolk, M.; Webster, S. *SID 02 Digest* **2002**, 784.

(17) Kroger, M.; Huske, M.; Dobbertin, T.; Meyer, J.; Krutwald, H.; Riedl, T.; Johannes, H.; Kowalsky, W. *Proc. of SPIE* **2005**, *5840*, 177.

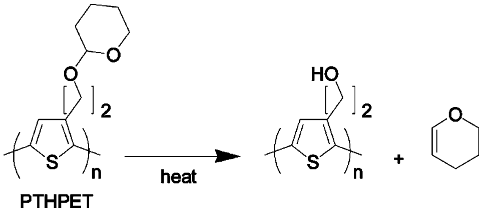
(18) Timpe, H. J. *IS&T's NIP 15: Int. Conf. Digital Print. Technol.* **1999**, *15*, 209.

(19) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.

(20) Blanchet. G.; Loo, Y.; Rogers, J. A.; Gao, F.; Fincher, C. R. *Appl. Phys. Lett.* **2003**, *82*, 463.

(21) Yu, J.; Holdcroft, S. *Macromolecules* **2000**, *33*, 5073.

Scheme 1. Thermolytic Reaction of PTHPET



30% weight loss is observed between 220 and 275 °C (Scheme 1). The weight loss is consistent with the deprotection scheme shown above. In conjunction with photoacid generators, chemically amplified photolithography of πCPs was also demonstrated.[21] In this paper we report on the thermal reaction of PTHPET induced by NIR irradiation and demonstrate direct thermal patterning of πCPs in which a soluble, thermally reactive polymer is converted to an insoluble polymer (Figure 1). The necessity of incorporating a NIR dye to achieve local heating and the resulting properties of the polymers are described together with the potential of direct thermal imaging as a high-throughput method for patterning πCPs.

Experimental Section

Regio-regular PTHPET with a head-to-tail content of $>$95%, as determined using NMR, was synthesized according to the general method described by McCullough and others.[21,22] Molecular weights of PTHPET measured against polystyrene standards were determined using gel permeation chromatography (Waters model 510) equipped with μ-Styragel columns. PTHPET and polystyrene were eluted with THF at a flow rate of 1 mL/min and detected with a UV−vis spectrometer (Waters model 486) at 440 nm. The NIR dye employed in this study was 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,1,3-trimethyl-2*H*-benzo[e]-indol-2-ylidene-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,1,3-trimethyl-1-*H*-benzo[e]indolium 4-methylbenzene-sulfonate (Figure 2) (FEW Chemicals) and the acid-sensitive molecular probe employed was 2-phenylquinoline (Aldrich) and was purified according to the literature procedure.[23]

Thermogravimetric analyses were performed on a Seiko Instruments Inc. TG/DTA 6300. Measurements were obtained at a heating rate of 5 °C/min on 5−8 mg of polymer/dye samples under ambient atmosphere. Variable temperature FT-IR spectra of drop-cast films on NaCl plates were recorded on a Nexus 670 series spectrometer coupled to a portable heater (Specac), temperature controller, and sample holder. Samples were held for 20 min in air at a given temperature prior to recording a spectrum.

Polymer films were spin-cast from chloroform for 30 s at 1500 rpm on 5 cm × 5 cm glass substrates (Corning). The thickness of the glass substrate was 0.95 mm. Patterns of PTHPET were obtained using a flat bed imaging laser scanner (Kodak Inc., Burnaby) which utilizes a NIR laser operating at a wavelength of 830 nm and a spot size of ~5 μm diameter. PTHPET patterns were typically obtained at a constant laser power of 23 W while varying the laser scan speed across the surface of the sample (0.3−0.7 m/s). Patterns were also obtained using 20−12 W power and a constant laser scan speed of 0.6 m/s. Exposed PTHPET films were developed by rinsing with methanol followed by THF. UV−vis absorption spectra were obtained with a Varian Cary 300 Bio spectrometer. Film thicknesses were determined using an Alpha-Step IQ surface profiler. Visible and fluorescent micrographs were obtained with a Nikon 50i Eclipse series microscope equipped with a 100 W mercury lamp and Q Imaging Qi-Cam 1394 digital camera. A Nikon (V-2A) fluorescence filter cube was employed, consisting of a dichromic mirror that permitted excitation wavelengths in the range of 380−420 nm to pass and prevented wavelengths ≤450 nm from reaching the detector/camera. Photoluminescent spectra and quantum yield measurements were obtained on a Photon Technologies International Quantum Master model QM-1 equipped with an integrating sphere.

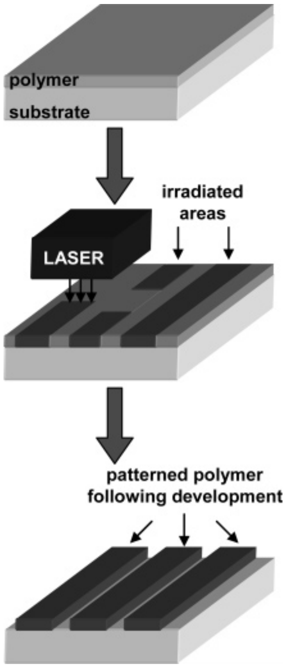


Figure 1. Schematic diagram for the direct thermal patterning of a πCP using a NIR laser.

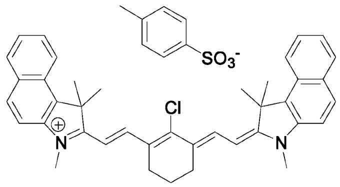


Figure 2. Molecular structure of the NIR dye used in this study.

The determination of acid content in films containing NIR dye was performed by preparing test films of poly(2-HEMA) containing the acid-sensitive molecular probe, 2PQ, and varying amounts of CSA. The poly(2-HEMA) and 2PQ solution was prepared by dissolving 33.9 mg of poly(2-HEMA) and 32.3 mg of 2PQ (1.6×10^{-4} mol) in 3 mL of methanol. To 500 μL aliquots of this polymer-probe solution was added 250 μL aliquots of CSA stock solutions, varying in acid concentration that ranged from 4.0×10^{-2} to 4.0×10^{-5} M CSA. The final solutions containing polymer, probe, and acid were then spin-cast at 1000 rpm for 30 s on quartz glass substrates. The UV−vis absorption spectra of the above films were then recorded.

Spin-cast PTHPET films containing NIR dye and the acid-sensitive probe were prepared by dissolving 4.0 mg of PTHPET (1.9×10^{-5} mol based on the polymer repeat unit), 4.5 mg of NIR dye (6.0×10^{-6} mol), and 5.1 mg of 2PQ (2.5×10^{-5} mol) into 333 μL of chloroform. The solution was filtered through a 0.2 μm syringe tip filter and spin-cast at 1500 rpm on quartz glass substrates. UV−vis absorption spectra were recorded before and after exposure to 830 nm laser light at energy dosages ranging from 1600 to 1200 mJ/cm^2.

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(22) Lowe, R. D.; Jayaraman, M.; Anderson, D. L.; McCullough, R. D. *J. Org. Chem.* **1993**, *58*, 904.

(23) Pohlers, G.; Virdee, S.; Scaiano, J. C.; Sinta, R. *Chem. Mater.* **1996**, *8*, 2654.

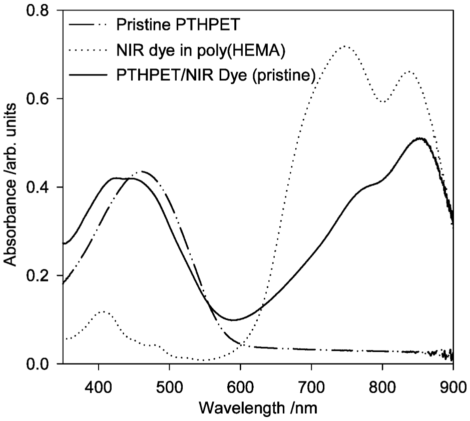

Figure 3. UV−vis absorption spectra of a pristine PTHPET film (solid-dotted line), pristine PTHPET film containing NIR dye (32 mol %, solid line) and a poly(HEMA)/NIR dye blend (dashed line).

Poly(2-HEMA) films containing 2PQ and varying amounts of NIR dye were prepared by dissolving ~2.6 mg of polymer, 4.5 mg of 2PQ (2.2×10^{-5} mol), and 1.5 mg or 14.4 mg of NIR dye (2.0×10^{-6} or 2.0×10^{-5} mol, respectively) into 300 μL of methanol. Solutions were spin-cast at 1500 rpm for 30 s on quartz glass substrates. UV−vis absorption spectra were obtained before and after patterning with 830 nm laser light at dosages ranging from 1200 to 1600 mJ/cm^2.

Results and Discussion

The UV−vis−NIR absorption spectrum of an ~80 nm thick film of PTHPET is shown in Figure 3. While the optical density at $\lambda_{max} = 463$ nm is 0.42 (38% transmittance), the absorbance of the polymer at 830 nm is <0.02, which is equivalent to >95% transmittance. The absorbance of this polymer is negligible at wavelengths >650 nm and is therefore unlikely to undergo localized heating upon irradiation with 830 nm NIR irradiation—in fact, all attempts to thermally deprotect the neat polymer using 830 nm irradiation were unsuccessful.

To achieve local heating with a NIR laser, PTHPET was molecularly doped with an NIR dye so that the optical density of the dye at this wavelength provides a significant but uniform absorption cross section. The NIR dye was chosen based on its physical and chemical properties: the dye is soluble in both chloroform and methanol and has a strong absorption profile between 650 and 900 nm with absorption peaks at 750 and 850 nm ($\epsilon = 250000$ M^{-1} cm^{-1} at 830 nm in chloroform). An absorption spectrum of the NIR dye dissolved in a poly(HEMA) film is shown in Figure 3. Poly(HEMA) was employed as a polymer support for the NIR dye solely for the purposes of obtaining a UV−vis−NIR absorption spectrum as the dye did not form uniform spin- or drop-cast films from solution. The dye also exhibits a relatively weak absorption near 410 and 450 nm which overlaps with the absorbance spectra of PTHPET.

The UV−vis−NIR absorption spectrum of a PTHPET/NIR dye film (mole ratio 2:1 based on the thienyl unit) spin-cast from a chloroform solution is shown in Figure 3. λ_{max} associated with the polymer (~450 nm) is blue-shifted with respect to the pristine polymer by ~10 nm. Weak absorption peaks of the NIR dye are visible at ~410 and ~450 nm as shoulders.

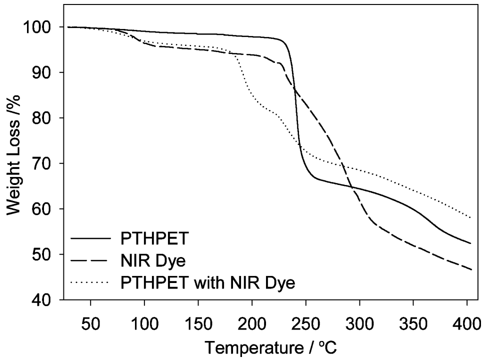

Figure 4. TGA thermograms of neat PTHPET (solid line), neat NIR dye (dashed line), and a PTHPET/NIR dye blend (32 mol % NIR dye, dotted line).

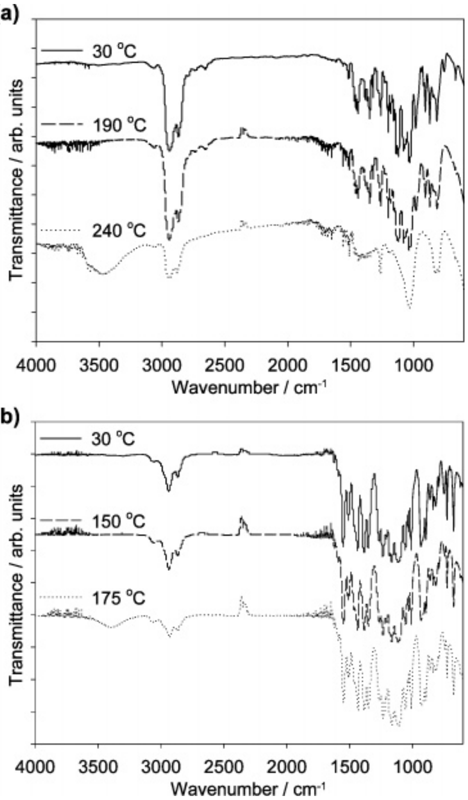

Figure 5. (a) FT-IR of PTHPET at 30, 190, and 240 °C. (b) FT-IR of a PTHPET/NIR dye film at 30, 150, and 175 °C.

Figure 4 (solid line) shows thermogravimetric analysis curves for PTHPET. PTHPET was found to undergo a ~36% loss in total mass at ~240 °C. This is consistent with the expected weight loss (40%) of THP via the release of dihydropyran. In the presence of NIR dye, PTHPET undergoes a thermal reaction at 170−180 °C as observed from Figure 4 (dotted line). The experimentally observed decrease in mass corresponding to loss of dihydropyran is 15%, which is consistent with the theoretical value of ~16%. The NIR dye itself thermally decomposes above 200 °C; hence, the dye does not prevent thermal reaction of the conjugated polymer. Rather, it lowers the temperature of the reaction, possibly by increasing the free volume of the polymer.[21]

The thermal reaction of PTHPET was verified using variable temperature FT-IR and the corresponding spectra can be found in Figures 5a and 5b. The evolution of FT-IR spectra for PTHPET films with increasing temperature correlates well with the information obtained from TGA experiments (see solid line in Figure 4) in that signals indicating the presence of OH groups (3400−3600 cm^{-1}) are absent at temperatures at 190 °C but present upon heating the film to 240 °C. FT-IR signals attributed to THP, found at 1200 and 1150 cm^{-1} (C−O−C antisymmetric stretch) and 650 cm^{-1} (O−C−O bending), are greatly diminished in intensity at 240 °C, which also indicates thermolysis of the polymer and loss of dihydropyran. In the presence of NIR dye, the emergence of a broad OH peak at ∼3450 cm^{-1} at ∼170 °C (Figure 5b) is consistent with the lower temperature of thermal reaction caused by the dye.

Neat films of PTHPET heated to 240 °C and composite films of PTHPET/NIR dye heated to 180 °C are rendered completely insoluble in organic solvents, whereas the unheated films are readily redissolvable. The reason for the change in solubility has been described previously[21] and is due to the loss of the bulky THP group, the increased H-bonding between polymer chains as a result of the formation of side chain hydroxyl groups, and the length of the hydroxyethyl side chains which are too short to solubilize a 2,5-linked polythienyl main chain. The change in polarity of the films due to the presence of the hydroxyl groups following thermal reaction is confirmed by the change in contact angle of water droplets on the surface from 90.7 ± 2.9° for pristine PTHPET films to 44.9 ± 1.5° for a PTHPET film heated above its deprotection temperature.

With the knowledge that the presence of the NIR dye in the PTHPET film results in a significant absorbance at 830 nm, that the polymer undergoes thermal reaction at <200 °C, and that resulting polymer films are rendered insoluble, films of PTHPET containing NIR dye were exposed to 830 nm irradiation from a NIR flat bed imaging laser scanner. The laser spot size was ∼5 μm in diameter and the laser power was varied between 12 and 20 W. The laser scan speed across the surface of a sample was varied between 0.3 and 0.7 m/s. The combination of laser power and scan speed determined the incident power striking the surface. Irradiated films were developed by rinsing with methanol and THF. Figure 6a shows optical micrographs of developed films. Feature sizes range from 50 to 280 μm in length and 11 to 45 μm in width. Line spacings between patterned polymer are as small as 10 μm and were easily resolved. Figure 6b shows an enlargement of the image showing the quality of a 10 μm resolution pattern. Figure 6c shows pixilated patterns of varying density—such variations in density are the basis for the formation of photographic quality images. The images illustrated were obtained with the laser operating at 20 W and a faster speed of 0.6 m/s so that the incident laser energy was ∼600 mJ/cm^2. Line edge sharpness as well as corners with near-right angles are maintained when laser scan speeds are held constant at rates as high as 0.6 m/s. To put the rapidity of this image process in context, the area of a letter-sized sheet may be imaged with 10 μm resolution in 10−20 s. Limitations of the imaging process are illustrated below: with maintaining of a constant laser power at 23 W and increasing of laser scan speeds from 0.3 to 0.7 m/s, developed patterns became distorted (see Figure 7). Patterns of PTHPET were successfully obtained with laser powers as low as 480 mJ/cm^2; however, the image quality was poor. In general, for the conditions and compositions described in this paper, exposing the film to laser fluences below 500 mJ/cm^2 gave poor quality images presumably due to insufficient heating of the polymer. Successfully patterned films required a high NIR dye content with a dye absorbance between 0.7 [20% T] and 0.8 [16% T] at 830 nm.

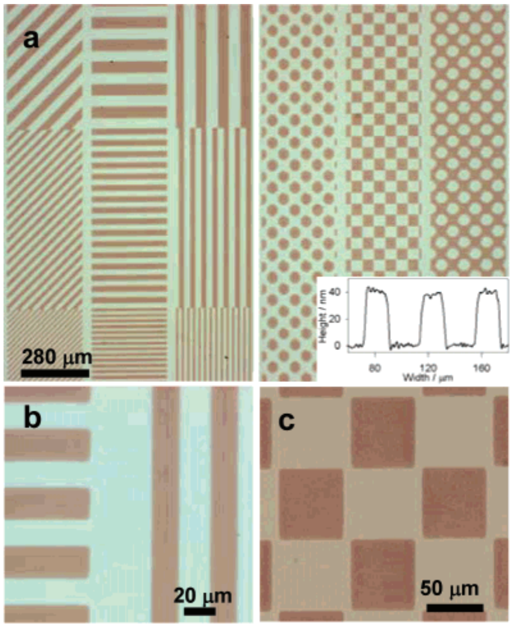

Figure 6. Bright field micrographs of a patterned film of polymer and NIR dye (32 mol %). (a) Line and pixilated structures (inset: surface profile); (b) higher magnification; (c) 50 μm pixilated structures. Incident laser energy was ∼600 mJ/cm^2.

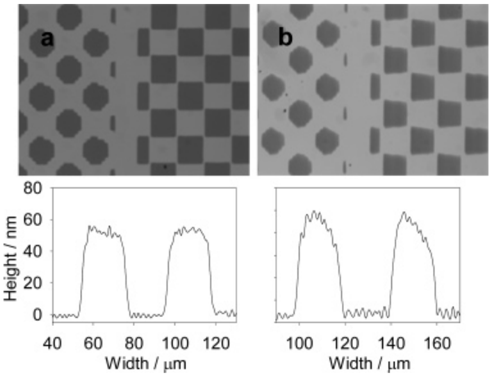

Figure 7. Monochromic microscope images of a patterned PTHPET film containing NIR dye obtained after laser exposure at various laser scanning speeds. Micrograph (a) patterned at a laser scan speed of 0.3 m/s and (b) 0.7 m/s. Laser power, 23 W.

Previous studies[13] have shown that >5 mol % of acid (camphorsulfonic acid) is needed to adequately deprotect PTHPET. Thus, based on the amount of PTHPET employed in the direct thermal patterning experiments (∼80 nm thick films), the minimum quantity of acid required for pattern transfer is ∼2.5 × 10^{-6} mol. To investigate the possibility that acid was inadvertently introduced into the film upon addition of the NIR dye, an experiment was devised and carried out using an acid-sensitive probe which, in the presence of acid, exhibits a strong UV−vis absorption response at 344 nm. UV−vis spectra of composite films containing NIR dye, PTHPET, and the probe indicated the absence of a peak at 344 nm. In test films consisting of just

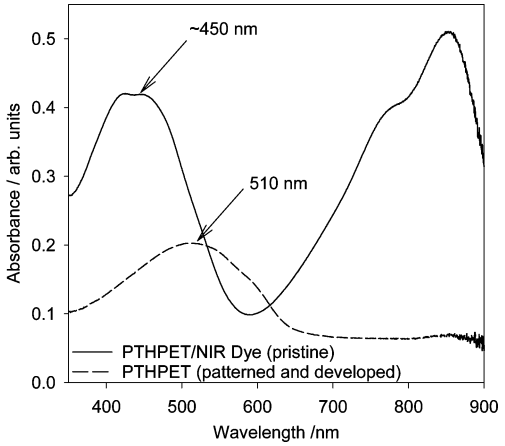

Figure 8. UV−vis−NIR absorption spectra of a pristine PTHPET/NIR dye film (solid line) and the patterned and developed film (dashed line). Film thickness, ~80 nm.

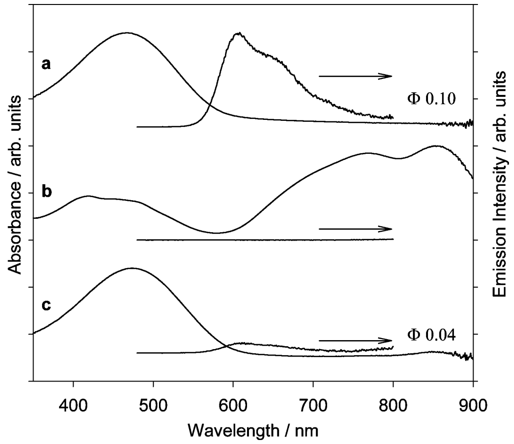

Figure 9. Absorption and photoluminescence spectra of (a) pristine PTHPET and (b) and (c) PTHPET containing NIR dye before and after methanol development. λ_{ex}, 460 nm.

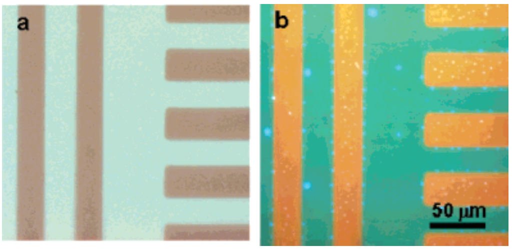

Figure 10. Bright field (a) and fluorescent (λ_{ex}, 380−420 nm, λ_{em}, >430 nm) (b) micrographs of a patterned PTHPET film. Incident laser energy, 600 mJ/cm^2 (20 W at 0.6 m/s).

the probe and camphorsulfonic acid in a poly(2-HEMA) matrix, it was found that the lower detection limit of acid for the system was 1.5×10^{-6} mol.

To investigate whether the NIR dye produced acid upon exposure to 830 nm laser light, poly(2-HEMA) films were prepared containing dye and an acid-sensitive molecular probe, 2PQ, and exposed to laser dosages ranging from 1200 to 1600 mJ/cm^2. A decrease in the NIR dye was observed between 600 and 900 nm, indicating that laser light was absorbed by the NIR dye but an increase in absorbance at 344 nm that would indicate the generation of acid and protonation of 2PQ was not observed. Therefore, it is concluded that the NIR dye does not introduce acid into the film.

Figure 8 shows UV−vis−NIR absorption spectra of PTHPET/NIR dye films before and after patterning and development. An interesting feature of the spectra is that λ_{max} of PTHPET prior to patterning and development is ~450 nm whereas after patterning it is 510 nm. Previous studies have shown thermolysis of PTPET films led to a red shift of their UV−vis absorption properties,[21] which was attributed to planarization of the main chain backbone due to the removal of the bulky THP group, thus allowing further extension of the conjugation length of the polymer. The red shift in the polymer observed in the present study is consistent with removal of the bulky THP group. Also of note is the absence of NIR dye in the patterned polymer film, indicating the developing procedure successfully removes most of the NIR dye.

Photoluminescent spectra of a pure PTHPET film and of PTHPET films containing dye before and after development are shown in Figure 9—the latter film was not patterned—it was only rinsed with methanol to remove dye. Values of λ_{max} (absorption) are 463, ~450, and 475 nm, respectively. λ_{max} corresponding to fluorescent emission from PTHPET is 605 nm. Quantum yields of fluorescence (Φ) for PTHPET films, with and without dye, are ~0.00 and ~0.10, respectively. Rinsing the NIR dye-containing film with methanol, so as to remove the dye, partially restored the quantum yield of emission to ~0.04 (Figure 9c), indicating that even though a majority of the dye has been removed, observed as a substantial decrease in dye absorption between 600 and 900 nm, residual NIR dye significantly quenches luminescence. The quantum yield of patterned and developed films of PTHPET was also lower than that of the pristine polymer films and is estimated to be <0.01. This value is low because of the increased coplanarity and hence π-stacking upon removal of the tetrahydropyranyl group. Also of note is that λ_{max} corresponding to the absorption of the PTHPET film red-shifts by ~25 nm when rinsed with methanol. The shift in PTHPET absorbance is most likely due to the increase in the free volume of the polymer film upon removal of the NIR dye so as to permit the conjugated polymer to relax from a contorted conformation to a more planar conformation. An increase in coplanarity of the polythienyl in the solid state also contributes to the reduced quantum yield of fluorescence.[24]

Fluorescent images of the patterned PTHPET film (orange areas of Figure 10b) were obtained with a fluorescence microscope using a broad band excitation source filter to provide 380−420 nm light; photoluminescent emission was recorded for wavelengths >430 nm. The photoluminescent emission intensity for PTHPET was low due to the poor overlap of the excitation energy (380−420 nm) with that of the patterned polymer (λ_{max}, 510 nm), and the thinness of the polymer pattern. Thus, a high background emission from the underlying substrate is observed.

Conclusions

A unique method for pixilation of π-conjugated polymers is presented. The technique, which employs novel chemistry

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(24) Han, X.; Chen, X.; Vamvounis, G.; Holdcroft, S. *Macromolecules* **2005**, *38*, 1114.

and state-of-the-art reprographic instrumentation, has the potential for producing high-resolution images with rapid throughput. Irradiation with 830 nm light of a thermally labile πCP, in the presence of NIR dye, results in the localized heating and causes a thermal reaction to occur. Absorbance spectra of PTHPET films containing NIR dye exhibited a blue shift in $\lambda_{\max}$ attributed to twisting of the polymer main chain, but upon patterning and development of the material, a red shift of absorption is observed due to increased planarization of the polymer backbone and which is attributed to liberation of dihydropyran and removal of the NIR dye from the film. Pixels of PTHPET are obtained with a resolution as low as 10 μm. The patterned material retains its fluorescence profile emission but there is a reduction in the quantum yield which is attributed to either the presence of residual NIR dye remaining in the film after development and/or coplanarization and chain aggregation after removal of the THP. Direct thermal patterning of highly fluorescent analogues of PTHPET is currently underway.

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