Photopatterned conjugated polymer electrochromic nanofibers on paper

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Abstract. Electrochromic nanofibers of conducting polymer (terthiophene) have been deposited over a conventional paper sheet by means of the electrospinning technique, and subsequently photopatterned by means of UV radiation. The synthesis of a processable precursor copolymer with a norbornylene matrix and pendant units of terthiophene makes the electrospinning process available, and allows for chemical or electrochemical crosslinking of the precursor copolymer to obtain a conducting polymer. The inclusion of photocrosslinkable units (methacrylate) in the precursor copolymer also allows for photopatterning of the material. This was applied to obtain patterns on the paper which can be chemically oxidized or reduced resulting in electrochromic characters. SEM images of the conducting polymer nanofibers together with the cellulose fibers show how these materials can be attached to textile fibers, adding new functionalities that are reminiscent of the chameleonic abilities of some living creatures.

1. Introduction

Increasing the processability of conducting polymers remains a focus of research in order that these materials may be introduced into mass production. Our group has developed a technique termed solid-state oxidative conversion (SOC)\cite{1}, which makes it possible to handle a processable precursor copolymer instead of an insoluble conducting product. The precursor polymer contains pendant units which will become the conducting polymer structure upon SOC. Once the precursor copolymer is deposited, the conducting polymer can be obtained either chemically or electrochemically. The SOC technique has been successfully applied, together with dip-pen nanolithography or e-spinning, to obtain nanostructures composed of conducting polymers (nanofibers and nanolines)\cite{2,3}. We report the inclusion of a photocrosslinkable unit in the precursor polymer structure so that it can be processed via any conventional photopatterning technique. As the technique does not have any limitations on the substrate used for these depositions, photopatterned electrochromic characters can be shown on conventional paper. These nanofibrous electrochromic polymers on paper, once converted by exposure to ultraviolet light, can be chemically switched between their oxidized and reduced states, thus causing a color change. The preparation of electrochromic paper is but one of many possible applications of this technique. Other potential used for a precursor approach towards the patterning of conducting polymers include the creation of microelectronic circuitry and electrochromic diffraction gratings. This simple, powerful, and versatile technique erases processability issues while encompassing a large swath of potential polymer and copolymer structures.
2. Experimental

2.1. Chemicals
Reactions were carried out in flame-dried flasks under N$_2$ atmosphere, unless noted otherwise. Anhydrous solvents (all of them from Aldrich Chemical Co.) were distilled over CaH$_2$ for all reactions. Deuterated chloroform (CDCl$_3$), 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP), ferric chloride and hydrazine were used as received from Aldrich Chemical Co. Grubb’s alkylidene catalyst was obtained from Strem Chemical and used without further purification.

2.2. Precursor copolymer synthesis
General structure of the precursor copolymer is shown in Scheme 1. The precursor copolymer PN3TMA6 (50 mol% of 5-norbornene-2-(methylene-3’-[2,2’:5’,2’”]-terthiophenecacetate) (NM3T), 6 mol % of 5-norbornene-2-methylene methacrylate (NMA) and 44 mol% 5-norbornene-2-acetoxymethyl (NA)) was synthesized as follows: NMA and NA were prepared according to literature.$^{[4]}$ A solution of N3T (1.0 g, 2.4 mmol), NA (0.35 g, 2.1 mmol), and NMA (0.056 g, 0.3 mmol) in anhydrous dichloromethane (20 mL) was cannulated into a vacuum-dried 100 mL Schlenk tube. Grubb’s alkylidene catalyst (0.02 g, 0.024 mmol) solution in dichloromethane (2 mL) was then cannulated into the reaction flask at room temperature. The reaction was quenched by adding 0.5 mL of ethyl vinyl ether. The reaction mixture was concentrated under vacuum and polymer was precipitated out in pentane (3x, 100 mL). Yield = 1.1 g (80%). Number-average molecular weight ($M_n$) of PN3TMA6 was found to be 85,350 g/mol (PDI = 1.617); $T_g$ of PN3TMA6 was found to be 55°C. Composition of PN3TMA6 was calculated using $^1$H-NMR with CDCl$_3$ solvent by integration value of aromatic protons [7.31 (b, 1H), 7.20-7.07 (b, 5H), 6.98 (b, 1H)] and olefinic protons [6.08 (b, 1H), 5.53 (b, 1H), 5.3 (b, 2H)].

2.3. E-spinning of nanofibers
The electrospinning of the nanofibers was made by applying 10.5 KV, at a distance of 10 cm, to a solution of 7% w/w precursor copolymer in CHCl$_3$/DMF(70/30%). Flow rate was 0.035 mL/hr.

2.4. Photochemical Crosslinking of PN3TMA6
As this precursor copolymer is soluble in many organic solvents, it can be processed using conventional techniques. The polymer contains pendant methacrylate groups which can be crosslinked photochemically, as shown in Scheme 1. Photochemical crosslinking of this precursor copolymer was performed by using 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP) as a photoinitiator and 365 nm UV-radiation.
Scheme 1: General structure of the precursor copolymers used. Photocrosslinking can be made by exposure of the methacrylate units to UV light. In these two steps, the polymer remains insulating. Further crosslinking to obtain a conducting polymer is achieved by either chemical or electrochemical oxidation of the terthiophene units.

Photochemical crosslinking via methacrylate groups was additionally confirmed by the sharp decrease in the FT-IR peak at 1640 cm$^{-1}$ attributed to the C=C stretch, compared to the initial polymer. This agrees with an earlier result for the crosslinking of both polynorbornylene and polycyclooctadiene that were derivatized with methacrylate units. Nanofibers were then converted to insoluble conductive polymer after photocrosslinking.

2.5. Chemical Solid-state Oxidative Conversion

Chemical oxidation of the terthiophene units of the previously photocrosslinked copolymer was made by immersion in a saturated ferric chloride acetonitrile solution. This results in the corresponding terthiophene conducting polymer, which can be chemically oxidized or reduced by immersing the polymer in saturated hydrazine and ferric chloride acetonitrile solutions, respectively.

2.6. Instruments

A CL-1000 UV Crosslinker (UVP) utilizing $\lambda = 365$ nm UV lamps with 5800 $\mu$w/cm$^2$ intensity was used for photopatterning. NMR spectra were obtained on a Bruker 400MHz spectrometer. FT-IR was done with a Nicolet Magna-IR 560 spectrometer.

3. Results and Discussion

3.3. Patterning Process

Conventional photopatterning techniques can be applied due to the presence of the photocrosslinkable methacrylate units in the precursor copolymer. Using the photocrosslinkable units, incorporated into the polymer backbone, one can make films or nanofibers of the soluble material on any substrate. The polymer film or fibers can then be selectively exposed to ultraviolet light using a photomask, thus creating insoluble regions on the patterned substrate (Figure 1). Development of the film or fiber mat results in a crosslinked negative of the photomask that is then later subjected to oxidative conditions either chemically or electrochemically, depending on the choice of substrate. After oxidative crosslinking, the crosslinked conductive polymer is in its oxidized state and can be redox switched to the reduced conjugated polymer state. Redox switching results in a change in color from blue to orange, and this process is reversible upon reversing the potential bias. Towards the creation of a truly flexible, paper-like
device, substrates such as polyethylene terephthalate (PET), PET-ITO, and common printer paper (cellulose) have been experimented with. Preliminary patterning results have shown the ability to make designs on each of these surfaces as illustrated for one case in Figure 2.

Figure 1: Scheme of the Photopatterning / solid-state oxidative crosslinking process

3.1. Chemical Solid state oxidative conversion

Once patterning was performed, chemical oxidation and reduction using ferric chloride and hydrazine, respectively, can be used to switch the electrochromic polymer from its colored to bleached states and back again. If patterning is achieved on a conducting substrate, it is also possible to electrochemically switch the polymer. Figure 2 shows the two color states of the nanofibers deposited and photopatterned on conventional paper (clear brown, almost transparent in their oxidized state and orange in their neutral state).

3.4. SEM characterization

Several SEM images of the photopatterned paper sheets were taken. They show how nanofibers of conducting polymer (average diameter between 100-200 nm) were deposited over cellulose fibers (or other fibers, like textile fibers), with the potential to change the properties of the resulting system. We have shown how the color properties can be modulated, with potential future applications in chameleonic fabrics. Figure 3 shows that the conducting nanofibers were deposited not only over the cellulose fibers, but also between them constituting a nanofibrous mat of hydrophobic material that will affect the porosity and wettability of the paper sheet.

Figure 2: Photopatterned conducting polymer nanofibers on paper showing colored characters.
4. Conclusion
The successful implementation of a new synthetic scheme towards the production of soluble, processable conducting polymers has been accomplished. The precursor approach allows for post-processing conversion to conducting material via solid-state oxidative conversion. The addition of a photocrosslinkable moiety further allows patterning of the precursor polymer to fit any microlithographic negative onto any one of numerous substrates. As a preliminary result, we have shown the deposition of nanofibers on conventional paper, and the subsequent photopatterning and chemical polymerization resulting in electrochromic characters. Application of this procedure over different substrates and the adequate materials can be beneficial in the design and improvement of electrochromic devices and electronics circuitry among others constituting our future work.

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