



Photopatterned electrochromic conjugated polymer films via precursor approach

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ABSTRACT

Herein we report the photolithography of electrochromic conjugated polymer (CP) films on the micron scale without exposing the CP to high energy UV radiation. The synthesis of polynorbornene-based precursor copolymers having units with pendant terthiophenes and photocrosslinkable units allows for photopatterning at an earlier stage with respect to the polymerization (chemically or electrochemically) that yields the conducting polymer. The effect that the composition of the photocrosslinkable unit has on the overall process was studied, showing no effect on the electrochemical and optical performance of the conducting polymer. Electrochromic photopatterned structures down to 1 μm were obtained, together with some basic structures for microelectronics. This technique does not have any specific substrate restrictions, and can be used to pattern conducting polymers on flexible, rigid, conducting, or insulating substrates using the present photolithography facilities available to industry and academia.

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1. Introduction

There is an increasing interest in substituting the conventional semiconductors present in electronic devices by conducting polymers, due to their chemical versatility, rapid processability under environmentally benign conditions and lower cost. Aside from the electronic conductivity of conducting polymers, their ability to reversibly change different properties (e.g. color, volume and/or stored charge) when undergoing redox processes is another highlight of these materials that has been used to develop a number of interesting electrochemical applications; these include electrochromic devices, artificial muscles and supercapacitors, among others. Some of these applications have been shown to greatly benefit from processing techniques that will decrease their overall size [1,2], which, in the case of electrochromics, would allow the creation of diffraction gratings or micrometer size pixels for color displays [3].

Patterning of conducting polymers in the micrometer range has been developed using several techniques, including photochemical lithography [4], scanning probe lithography (SPL) [5,6], micro-molding [7], electropolymerization using modified electrodes [8], line patterning [9], and printing techniques [10]. The interests for photolithography lie in large-area and high-volume applications, due to the fast processing speed, low cost, and low temperature

requirement of this technique. However, photolithography of conducting polymers faces two main problems: insufficient processability of the conducting polymers which remains a general problem for other deposition techniques as well and the degradation of the polymer due to high energy radiation which will lead to detrimental effects on the electrochemical and electronic properties of the material.

Several different approaches have been explored in order to improve the processability of conducting polymers, such as derivatization of the conducting polymer backbone [11], a template approach for making CPs water-processable [12], use of an alkyl substituted monomer [13], and a processable polymer backbone having pendant heterocyclic moieties [14]. Our group has introduced a technique that offers the advantage of having a processable precursor polymer than can be deposited via conventional techniques such as dip, spin, and spray coating [15,16]. Since the precursor route offers a conventional polymer backbone structure and is prepared using traditional polymerizations, the polymer backbone is flexible and can be of a high degree of polymerization thereby offering properties such as low glass transition temperatures relative to conjugated polythiophenes and processing procedures such as embossing and spinning of fiber. The precursor polymer is then converted to conducting polymer, in the solid state, while maintaining the cast form of the polymer in approximately quantitative yield while maintaining surface morphology. This solid-state oxidative crosslinking process has been successfully demonstrated for the direct nano-writing of conducting polymers using an atomic force microscope tip as the working electrode [17], nano-imprint lithography to generate nanometer periodic structures [18] and for the preparation of welded electrochromic nanofibers [19].

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Previously reported photopatterning of conducting polymers mostly involves the conversion of an insulating polymer to a conducting polymer on exposure to high energy radiation [20,21]. Other methods involve the selective degradation (photobleaching) of the exposed portion to achieve the negative pattern on the substrate [22]. The photolithography of poly(3-alkylthiophene)s has also been studied using selective crosslinking via the exposed alkyl group [23]; a copolymer approach has also been tried with polythiophenes having a cinnamoyl group, but the process involves exposure of conducting polymers to high energy UV radiation, which may cause photochemical damage to the conducting polymers [24].

Herein, we describe a simple, conventional photochemical patterning of an electrochromic conducting polymer using solid-state oxidative crosslinking that does not involve UV exposure to the conducting polymer. Ring opening metathesis polymerization (ROMP) is used to obtain precursor copolymers having units with pendant terthiophene and units with pendant photocrosslinkable moieties. The process involves the photopatterning of the insulating precursor copolymer via photochemical crosslinking through the methacrylate or cinnamate units. In this method, the UV radiation is applied before the polymerization of the terthiophene units, which is carried out afterwards by means of chemical or electrochemical solid-state oxidative crosslinking, resulting in a conjugated polymer. The photopatterning of the precursor polymers communicated herein can be used in combination with our direct-write nanolithography, nanofiber mats, and nanoimprint lithography to rapidly generate conjugated polymers having both micrometer and nanometer periodic structures.

2. Experimental

2.1. Chemicals

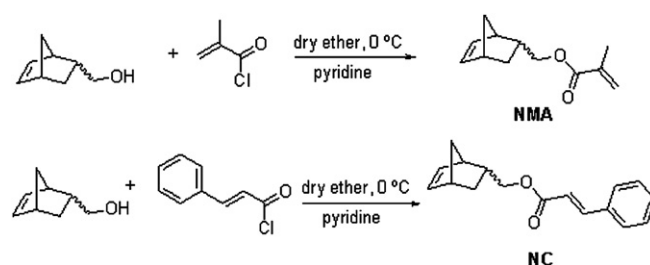
Anhydrous solvents were distilled over calcium hydride for all reactions before use in electrochemical and optical studies. Methacryloyl chloride and cinnamoyl chloride were purchased from Aldrich Chemical Co. and distilled under nitrogen prior to use. 5-Norbornene-2-methanol, 2,2-dimethoxy-2-phenyl-acetophenone and deuterated chloroform (CDCl_3) were used as received from Aldrich Chemical Co. Antimony (V) chloride and Grubb's alkylidene catalyst were purchased from Acros Chemicals and Strem Chemicals, respectively, and used without further purification. Tetrabutylammonium perchlorate (TBAP) was synthesized by drop-wise addition of perchloric acid into a tetrabutylammonium bromide solution in water at 0°C followed by recrystallization in ethanol and drying at 60°C in a vacuum oven for 24 h. Proper care must be taken when handling perchloric acid and their salts, as explosion may occur upon heating.

2.2. Monomer synthesis

All reactions were carried out in flame-dried flasks under nitrogen atmosphere unless stated otherwise. 5-Norbornene-2-(methylene-3'-[2,2':5',2'']-terthiophene acetate) (NM3T) and 5-norbornene-2-acetoxymethyl (NA) were synthesized according to the literature procedure [19]. 5-Norbornene-2-methylene methacrylate (NMA) and 5-norbornene-2-methylene cinnamate (NC) were synthesized by treating norbornene-2-methanol with methacryloyl chloride and cinnamoyl chloride, respectively, in the presence of pyridine as shown in Scheme 1. Monomers were characterized by ^1H NMR, ^{13}C NMR, FT-IR and GC-MS.

2.2.1. 5-Norbornene-2-methylene methacrylate (NMA) synthesis

Methacryloyl chloride (4.8 g, 46 mmol) was added drop-wise to a vacuum dried 100 mL 3-neck flask containing a solution of 5-norbornene-2-methanol (2.84 g, 23 mmol) in anhydrous diethyl



Scheme 1. Preparation of 5-norbornene-2-methylene methacrylate (NMA) and 5-norbornene-2-methylene cinnamate (NC).

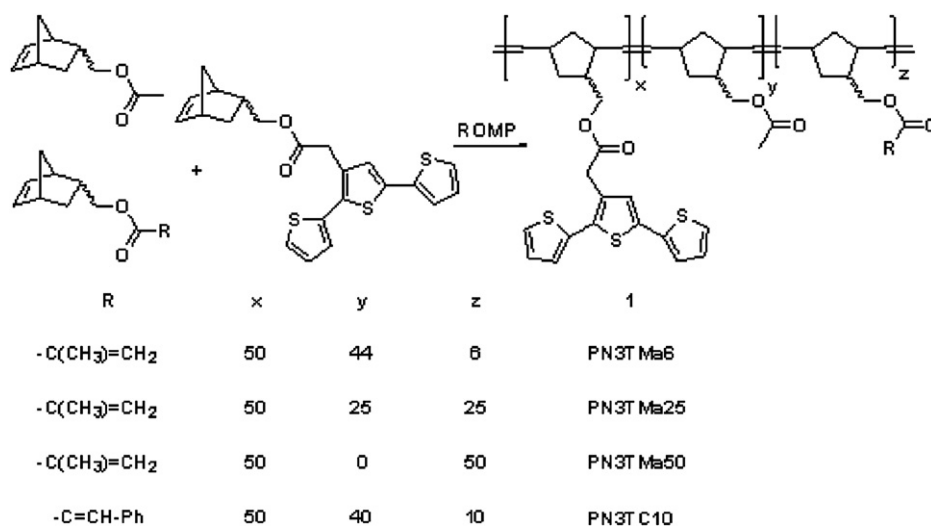
ether (200 mL) and pyridine (3.63 g, 46 mmol) while stirring under nitrogen at room temperature. After complete addition, the reaction continued at room temperature for 10 h and was then quenched by pouring the reaction mixture into a beaker containing cold water (200 mL). The mixture was extracted with diethyl ether (3 times, 50 mL each), and the ether layer was washed with water (2 times, 100 mL each), 1 N HCl (2 times, 100 mL each), and again with water (2 times, 100 mL each). After drying over anhydrous MgSO_4 , the mixture was concentrated under vacuum. The resulting crude product was purified by liquid-column chromatography (dichloromethane) to afford a colorless oil (3.5 g, 80%). GC-MS: m/z 192 (M^+); ^1H NMR (CDCl_3 , δ ppm), endo:exo 7:3 mixture, endo isomer: 6.16 (dd, 1H), 6.11 (m, 1H), 5.95 (dd, 1H), 5.55 (m, 1H), 3.94 (dd, 1H), 3.70 (dd, 1H), 2.90 (b, 1H), 2.83 (b, 1H), 2.44 (m, 1H), 1.95 (s, 3H), 1.85 (m, 1H), 1.45 (dd, 1H), 1.25 (d, 1H), 0.54 (dt, 1H); exo isomer: 6.11 (b, 3H), 5.55 (m, 1H), 4.23 (dd, 1H), 4.04 (dd, 1H), 2.83 (b, 1H), 2.73 (b, 1H), 1.95 (s, 3H), 1.74 (m, 1H), 1.33 (b, 2H), 1.25 (d, 1H), 1.19 (dt, 1H); ^{13}C NMR (CDCl_3): 167.5, 137.6, 136.9, 136.6, 136.2, 132.2, 125.3, 125.2, 68.7, 68.0, 49.4, 45.0, 43.9, 43.7, 42.0, 41.6, 38.0, 29.5, 28.9, 18.4; FT-IR (cm^{-1}): 3057 cm^{-1} (vinyl C-H stretch), 2974 and 2867 cm^{-1} (aliphatic C-H stretch), 1719 cm^{-1} (ester C=O stretch), 1636 cm^{-1} (aliphatic C=C stretch), 1450 cm^{-1} ($-\text{CH}_3$ antisym deformation), 1331 cm^{-1} ($-\text{CH}_3$ sym deformation), 1295 cm^{-1} (ester C-C-O stretch).

2.2.2. 5-Norbornene-2-methylene cinnamate (NC) synthesis

Cinnamoyl chloride (1.34 g, 8.0 mmol) was taken in a vacuum dried 250 mL 3-neck flask and anhydrous diethyl ether (100 mL) was cannulated into the flask. A solution of 5-norbornene-2-methanol (1.0 g, 8.0 mmol) in anhydrous ether (10 mL) was added to the above solution drop-wise via syringe at room temperature with continuous stirring. The reaction was allowed to continue at room temperature for 9 h, and was followed by quenching with water (100 mL). The ether layer was collected and dried with magnesium sulfate before evaporating the solution. The product was purified by liquid-column chromatography using dichloromethane as an eluent. GC-MS: m/z 254 (M^+); ^1H NMR (CDCl_3 , δ ppm), endo:exo 3:2 mixture, olefinic and aromatic protons: 7.7 (d, 1H), 7.34 (dd, 1H), 7.23 (dd, 1H), 7.20 (dd, 1H), 7.18 (dd, 1H), 7.13 (s, 1H), 7.09 (m, 1H), 7.01 (dd, 1H); endo isomer: 6.15 (dd, 1H), 5.92 (dd, 1H), 3.91 (dd, 1H), 3.74 (s, 2H), 3.70 (dd, 1H), 2.83 (b, 2H), 2.38 (m, 1H), 1.83 (ddd, 1H), 1.42 (dd, 1H), 1.25 (d, 1H), 0.54 (dt, 1H); exo isomer: 6.07 (b, 2H), 4.23 (dd, 1H), 4.04 (dd, 1H), 3.76 (s, 2H), 2.83 (b, 1H), 2.68 (b, 1H), 1.74 (m, 1H), 1.36–1.29 (b, 3H), 1.17 (dt, 1H); ^{13}C NMR (CDCl_3): 170.7, 137.6, 136.9, 136.8, 136.2, 135.9, 134.9, 132.2, 132.1, 130.9, 127.9, 127.8, 126.8, 126.7, 126.2, 124.7, 123.9, 69.2, 68.6, 49.4, 45.0, 43.9, 43.7, 42.3, 41.8, 38.0, 37.8, 35.1, 30.9, 29.6, 29.0; FT-IR (cm^{-1}): 3120 and 3080 cm^{-1} (aromatic and vinyl C-H stretch), 2985 and 2993 cm^{-1} (aliphatic C-H stretch), 1734 cm^{-1} (ester C=O stretch), 1259 cm^{-1} (ester C-C-O stretch).

2.3. Precursor polymer synthesis

Norbornene-based copolymers and terpolymers were prepared from NM3T, NA, and NMA or NC monomers via ROMP using Grubb's



Scheme 2. Synthesis of the precursor copolymers via ROMP.

alkylidene catalyst and triphenyl phosphine (5 moleq. wrt catalyst). Triphenyl phosphine was added in order to achieve polymers with low molecular weight distributions (PDI) as demonstrated earlier by Grubbs and Bielawski [25]. Different copolymers and terpolymers were synthesized (Scheme 2) by varying NMA (or NC) (6, 10, 25, 50 mol%) and NA compositions while keeping the NM3T composition (50 mol%) constant to study the effect of NMA composition on the physical, electrochemical and optical properties of the polymer (e.g. precursor polymer with 6 mol% of NMA (PN3T Ma6), was synthesized by the following procedure: a solution of NM3T (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 to a vacuum dried 100 mL Schlenk flask. 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, and allowed to react for 1 h 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 (3 times, 100 mL each). Yield = 1.1 g (80%). Copolymer and terpolymer compositions were determined via ¹H NMR using aromatic protons at $\delta \sim 7.0$ ppm, corresponding to one of the protons in terthiophene units, and olefinic protons at $\delta \sim 5.3$ ppm and 6.1 ppm, corresponding to cyclopentyl and methacrylate or cinnamate units, respectively (Scheme 2). Glass transition temperatures (T_g) and molecular weights of polymers are shown in Table 1. The T_g of the precursor polymers was found to decrease slightly with an increase in NMA composition. The precursor, PN3TC10, has a slightly higher T_g due to the bulky cinnamate group.

2.4. Electrochemical and chemical solid-state oxidative crosslinking

A platinum button electrode (2 mm diameter) was used as the working electrode along with a Pt flag counter electrode (1 cm²) with an Ag/Ag⁺ (non-aqueous, 0.456 V vs. NHE) reference electrode. Electrochemical solid-state oxidative crosslinking was

performed by scanning a potential range from 0 V to +0.8 V at a scan rate of 50 mV s⁻¹ in a 0.1 M TBAP/ACN solution. For opto-electrochemical measurements, cuvette-sized ITO glass was used as the working and counter electrodes. ITO glass (unpolished float glass, $R_s = 15\text{--}25 \Omega$) was purchased from Delta Technologies Inc.

2.5. Equipment

A CL-1000 UV crosslinker (UVP) equipped with 365 nm wavelength UV lamps with an intensity of 5800 $\mu\text{W}/\text{cm}^2$ was used. An optical microscope was used to observe the color of the conjugated polymer pattern during electrochemical switching between oxidized and neutral states, and a CH Instruments 400 potentiostat was used for all electrochemical studies. Optical properties were studied with a Perkin-Elmer Lambda 900 UV-vis-NIR spectrophotometer equipped with UV Winlab software. A four-point collinear array technique was used to measure conductivity by applying a current across the outer leads using a Keithley Instruments 224 constant current source, and measuring a voltage difference between the two inner leads using a Keithley Instruments 2700 multimeter.

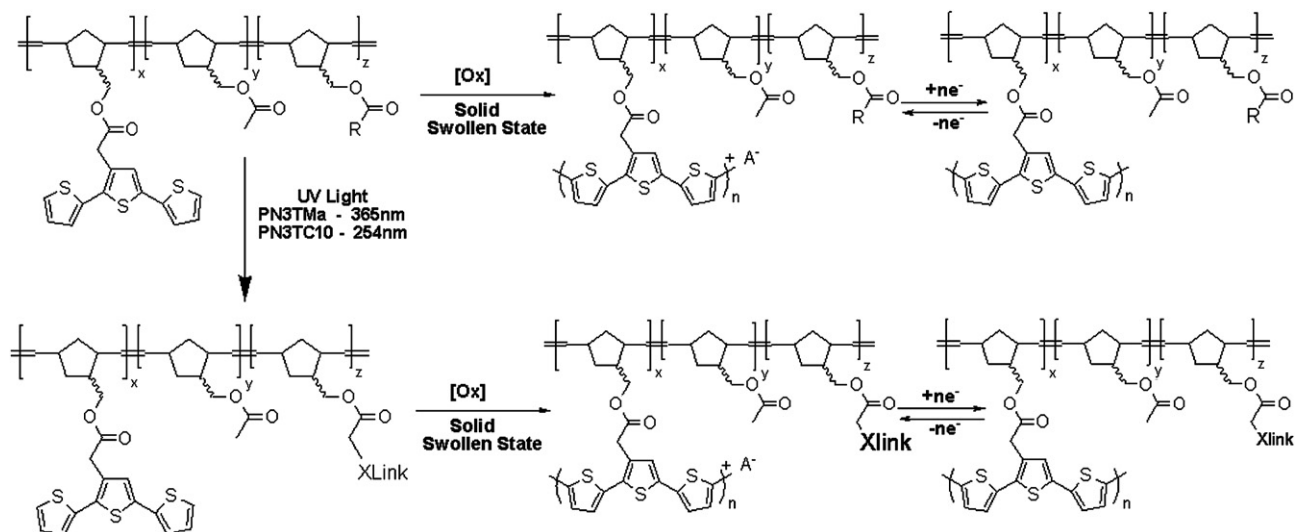
3. Results and discussion

3.1. Obtaining photocrosslinkable precursor copolymers

As we reported earlier [15–19], the solid-state oxidative crosslinking process makes use of a polynorbornene backbone with attached oligothiophenes. The precursor polymer at that stage can be processed by conventional techniques such as spin-coating, drop-casting, electrospinning, etc. Subsequently, the film can be subjected to chemical or electrochemical oxidation while in the solid swollen state maintaining the uniformity of the coated film. Different pendant groups can be attached to the norbornene backbone in order to obtain different electro-optical properties. Scheme 3 summarizes the overall process. In the present study, methacrylate- or cinnamate-based units were attached in order to get photocrosslinkable precursor copolymers for the solid-state oxidative crosslinking process. Unlike acrylate, a beneficial property of cinnamate is its thermal stability up to 210 °C. 5-Norbornene-2-(methylene-3'-[2,2':5',2'']-terthiophene acetate) (NM3T), 5-norbornene-2-acetoxymethyl (NA) and 5-norbornene-2-methylene methacrylate (NMA) [or 5-norbornene-2-methylene cinnamate (NC)] were synthesized and used to obtain copolymers with

Table 1
Molecular weight (M_n), PDI and T_g of precursor copolymers

Polymer	M_n	PDI	T_g (°C)
PN3T Ma6	85,400	1.17	55
PN3T Ma25	149,300	1.35	52
PN3T Ma50	38,900	1.18	48
PN3TC10	77,100	1.14	58



Scheme 3. Conversion of the precursor copolymer to the oxidized or neutral forms of the conducting polymer. Conversion of the precursor copolymer to a crosslinked state is made via UV radiation, while conversion from the crosslinked precursor to the conjugated polymer can be made by chemical or electrochemical solid-state oxidative crosslinking. Subsequent redox processes allow to reversibly obtain the oxidized and neutral forms of the conducting polymer.

different composition ratios, namely 6, 10, 25 and 50 mol% of the photocrosslinkable groups. Photochemical crosslinking of the precursor copolymers having pendant methacrylate was performed using 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP) as a photoinitiator and UV radiation of 365 nm for all reported studies; the photochemical crosslinking of the precursor copolymer having pendant cinnamate was performed by irradiation with 254 nm light without use of a photoinitiator. The photocrosslinked precursor copolymers were insoluble in organic solvents, like chloroform, methylene chloride, and THF.

Photochemical crosslinking via methacrylate groups was further confirmed by the sharp decrease in the FT-IR peak at 1640 cm^{-1} corresponding to C=C stretch as compared to the starting polymer. This is in agreement with an earlier reported result for the crosslinking of both polynorbornylene [26] and polycyclooctadiene [27] having pendant methacrylate units. Photochemical crosslinking via the cinnamate groups was also confirmed by the sharp decrease in the FT-IR peak at 1713 cm^{-1} corresponding to C=O stretch as compared to the starting polymer. All precursor polymers containing different compositions were converted into insoluble polymer after photocrosslinking.

3.2. Effect of adding photocrosslinkable groups on conducting polymer performance

Electrochemical or chemical solid-state oxidative crosslinking has been previously carried out under a number of conditions, including electrochemical atomic force microscopy (AFM) [15–19]. In order to ensure the availability of the process using the aforementioned new copolymers, the effect that the composition of the photocrosslinkable groups present in the precursor copolymer structure has on the subsequent solid-state oxidative crosslinking process was investigated.

Electrochemical solid-state oxidative crosslinking and subsequent cycling of the obtained conducting polymer were carried out for all previously described copolymers, both before and after crosslinking, resulting in similar electrochemical responses (Fig. 1). The incorporation of NMA (or NC) and NA groups has no effect on the subsequent photochemical crosslinking or on the electrochemical solid-state oxidative crosslinking process. This was observed for copolymers containing up to 50 mol% of crosslinkable group in the precursor copolymer structure.

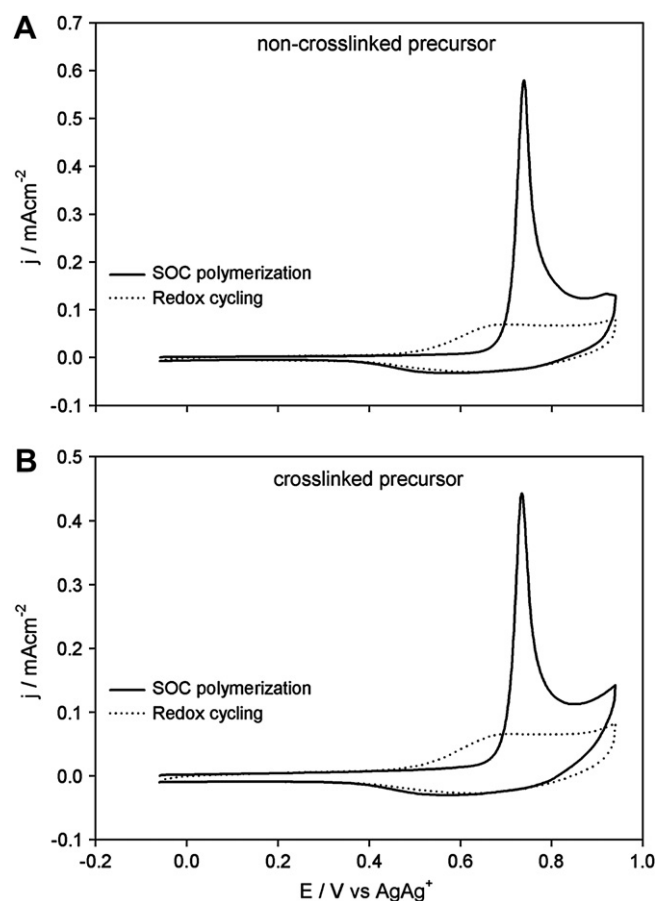


Fig. 1. Electrochemical polymerization of the precursor copolymer and subsequent cycling of the resulting conducting polymer for a (A) non-crosslinked precursor copolymer and (B) photocrosslinked copolymer. In both cases, solid lines represent the polymerization cyclic voltammogram (CV) and dashed lines show the subsequent cycling of the conducting polymer. CVs shown correspond to a 6 mol% methacrylate containing precursor copolymer. Experiments were carried out in a 0.1 M TBAP/acetonitrile solution, at 50 mV s^{-1} , using a platinum button electrode as the working electrode (2 mm diameter) and another platinum sheet ($S=1\text{ cm}^2$) as a counter electrode. Potentials are referred to an Ag/Ag⁺ non-aqueous reference electrode (0.456 V vs. NHE).

Additionally, chemical oxidative crosslinking was carried out by dipping the precursor coated glass into a 0.01 M iron(III) chloride solution to convert the colorless precursor copolymers into blue colored conjugated polymer films. This color transition is an indication of oxidized polyterthiophene. Subsequent reduction by immersion in a 0.01 M hydrazine solution resulted in orange colored films, corresponding to the neutral form of polyterthiophene. The process was carried out for different films before and after the photocrosslinking of the precursor copolymers and no significant differences in the optical spectra were found for the oxidized or neutral forms of the conducting polymer. Values of λ_{\max} , λ_{onset} for the π to π^* transition, and band-gap energies in their neutral form of the crosslinked conjugated polymers with varying compositions were obtained, showing no significant differences. Values of λ_{\max} for increasing mole percent compositions of the crosslinking moiety (6, 10, 25 and 50, respectively) were found to be 444, 440, 424, and 421 nm. Values of λ_{onset} for π to π^* transition were 572, 569, 554 and 554 nm, respectively. Corresponding band-gap energies were 2.17, 2.19, 2.24 and 2.24 eV. The shift of the λ_{\max} to higher energy may be a result of the limited conjugation length that can be obtained as a result of there being a higher crosslink density. Fig. 2 shows the absorbance spectra of the crosslinked precursor copolymer, together with the oxidized and reduced forms of the corresponding conjugated polymer.

Conductivity measurements were performed and in all cases, the values were on the order of $10^{-2} \text{ S cm}^{-1}$ for varying amounts of NMA (or NC) compositions, demonstrating that there is no effect of photochemical crosslinking on the conductivity of the resulting polyterthiophene.

3.3. Photopatterning of the conducting polymer

The precursor copolymer films are photochemically crosslinked via methacrylate or cinnamate groups by selectively blocking the UV radiation with a photomask (Fig. 3). After development with chloroform, a negative of the photocrosslinked precursor polymer is obtained; it is then oxidatively crosslinked to give a polyterthiophene network. Sets of $40 \mu\text{m}$ width polyterthiophene lines were patterned using the technique described above, and these were switched electrochemically between blue (oxidized) and orange (neutral) as shown in Fig. 4A. With the described procedure, films of polyterthiophene were obtained on ITO glass, glass or polyethylene terephthalate (PET) (Fig. 4). Terthiophene, according to spectrophotometric data, was stable during the photochemical

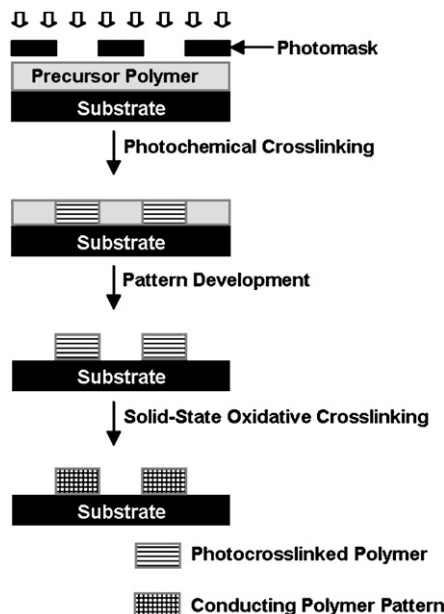


Fig. 3. Photochemical crosslinking followed by solid-state oxidative crosslinking to obtain conducting polymer patterns.

crosslinking step. We anticipate that many other heterocycles, apart from terthiophene, can also withstand UV exposure without undergoing undesirable reactions and can therefore be used in this unique photopatterning process for, ultimately, the formation of conductive polymer micropatterns.

Potential market-oriented applications of photopatterned conducting polymers include electrochromic devices as well as uses for the semiconducting functionality of the resulting materials. We demonstrate (Fig. 4A) $40 \mu\text{m}$ patterned electrochromic lines and $1 \mu\text{m}$ patterned dots (Fig. 4B). With these dimensions being well below the resolution limit of the human eye, one could conceive of pixelated mats for organic-based displays, in which the full color gamut is obtained using different integrated polymers having basic RGB properties. This technique could show promise in the electronics industry. Taking into account that most electronic devices are made by the stepwise deposition of different materials and that the deposition steps mainly involve the solution casting of a polymeric layer, in the case of organic devices. Generally, photochemical crosslinking has been used to make each layer resistant to the solvent used for the deposition of the subsequent layer. We believe that our photopatterning process will aid in the deposition of different electroactive polymer multilayers, followed by a one-step swollen solid-state oxidative crosslinking process to produce multilayer electronic devices.

4. Conclusions

A new method for obtaining photopatterned conductive polymers has been shown and potential applications in the construction of organic-based electrochromic or electronic devices have been discussed.

Photocrosslinkable units of methacrylate or cinnamate have been copolymerized with a norbornene structure containing pendant terthiophene units. This precursor copolymer is processable and can be deposited in a number of ways, including spin-coating, drop-casting or any other conventional technique. The resulting film can be photocrosslinked and thus conventional patterning techniques can be applied. The terthiophene pendant units present in the photocrosslinked polymer can be polymerized by a solid-state oxidative crosslinking process, using conventional

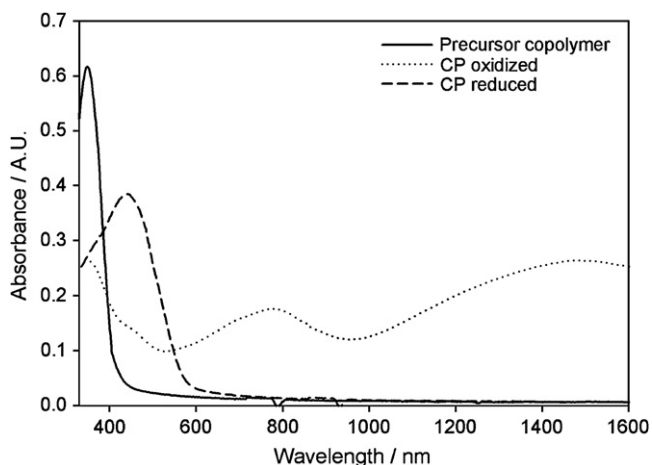


Fig. 2. UV-vis-NIR spectra of the crosslinked precursor copolymer and the oxidized and reduced forms of the corresponding conjugated polymer (CP). Data shown correspond to a 6 mol% methacrylate containing precursor copolymer and the resulting conjugated polymer.

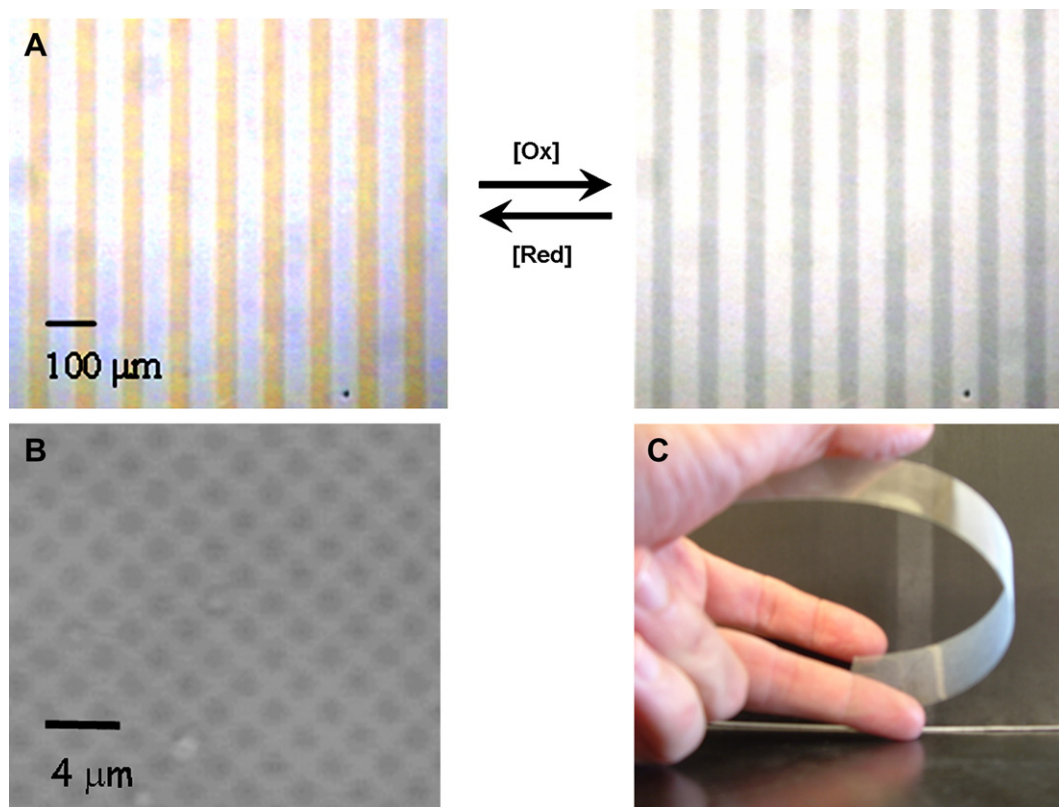


Fig. 4. Micropatterns of conducting polymer: (A) 40 mm width patterned electrochromic lines over ITO glass. The obtained polyterthiophene shows a blue color in its oxidized state (+0.8 V) and an orange color in its neutral state (+0.3 V). Potential values are referred to an Ag/Ag⁺ non-aqueous reference electrode (0.456 V vs. NHE). (B) The 1 μm dots array, photocrosslinked over quartz. (C) The technique presented herein allows different substrates to be used. The picture shows the precursor copolymer deposited onto an insulating, flexible substrate (polyethylene terephthalate (PET)) (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

electrochemical or chemical techniques, resulting in polyterthiophene patterned structures. The composition of the photocrosslinkable units in the precursor copolymer was shown to have no effect in the overall process. The resulting conducting polymer retained all of its electrochemical properties, even for 50 mol% of the photocrosslinkable unit. The 40 μm patterned electrochromic lines and the 1 μm patterned dots were shown, with potential applications in electrochromic devices below the resolution of the eye (potentially useful for RGB full color pixel mats), as well as basic structures for organic electronic devices.

Working with a photocrosslinked precursor polymer instead of a linear structure broadens the potential range of solvents for the subsequent solid-state oxidative polymerization, taking into account that the crosslinked precursor won't be easily dissolved in it, but swollen. The choice of adequate solvents, together with control over the composition of the photocrosslinkable unit, may result in an enhanced control over the final dimensions of the patterned structure. Swollen structures after the photopatterning process may then result in controlled, smaller dimension patterns than the previous pattern, thus allowing an increase in the resolution of the present nanolithography techniques. Combining photopatterning with electrochemical atomic force microscopy and nanoimprint lithography and combination with electrostatic spinning to rapidly generate both microstructures and nanostructures is currently underway.

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