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Photochemical polymerization of thiophene derivatives in aqueous solution†

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A novel method of photochemical polymerization of thiophene derivatives in aqueous solution catalyzed by potassium dichromate and initiated by illumination is described.

Polythiophenes have been a subject of intensive research during the last two decades. These materials, containing a π-conjugated carbon backbone, exhibit a number of interesting electrochemical, electrochromic and shielding properties, that together provide a basis for various new technologies.[1–3] Thiophene derivatives can be oxidized chemically,[2,4,5] photochemically[3,6–8] or electrochemically[1] and polymerized to the corresponding oligo- or polythiophenes. However, the processability of those materials is rather poor which impedes their practical application. In particular their solubility in most organic solvents and water is too low. An intensive research effort has been initiated aimed at the development of highly soluble and easily processable polythiophenes including for example alkylsulfanyl groups,[4] to render the polymer soluble in organic solvents or carboxylic[2] or sulfonic[5] acids to confer water solubility. Despite the progress achieved in these studies, the yield of polythiophenes is often low and the process itself can be expensive and demand the use of aggressive and toxic solvents.

We report here on the photopolymerization of some substituted thiophenes, namely 3-thiophene acetic acid (TAA), boronic acid (TBA) and carboxylic acid (TCA), catalyzed by potassium dichromate. This reaction can be performed under mild conditions in an aqueous environment and using irradiation with visible light. The process leads to a high yield of oligomers (4–7 mers), which are soluble in THF and the simultaneous deposition of insoluble polymer on the illuminated surface. Previous work within this department has shown the suitability of this process for making molecularly imprinted films for use in assays.[9] A typical polymerization, that of TCA was performed as follows: 10 mmol of 3-thiophenecarboxylic acid were dissolved in 50 ml of deionized water and mixed with 50 ml of 30 mmol aqueous potassium dichromate. The solution was exposed to visible light (100 W) for 3 days. During the steady state irradiation with visible light, the solution became brown in colour, forming a dark brown precipitate and coating on the illuminated container surface. This was not observed when reactions were carried out in the dark, or when potassium dichromate was replaced by copper(II) chloride, ferric chloride, potassium permanganate or ammonium persulfate. The resulting suspension was evaporated and the brown residue washed extensively with water to remove non-reacted monomer and potassium dichromate. After drying the oligomers were extracted with refluxing THF. The yield of the oligomeric derivatives was 85%. The same reaction was performed in polystyrene cuvettes ($10 \times 10 \times 45$ mm^3, Sarstedt, Germany) which were used for measuring the UV-vis absorbance of the deposited film or in polycarbonate Petri dishes. Similar behaviour was found when TAA or TBA were used as the monomers.

Elemental analysis of the soluble fraction of polythiophene carboxylic acid gave: C 37.7%; H 2.8%; S 16.4%; Cr 12.8%; K 0.5%. The lower value of the S/C ratio (0.44) compared to the theoretical one (0.53) is due to bond breaking of thiophene rings.[7] Unfortunately it proved impossible to remove the chromium contaminant (Cr_2O_3). Various methods were attempted, but only the most drastic such as hot alkaline persulfate solution removed Cr. However this also appeared to affect the polymer composition, probably due to further oxidation.

GPC analysis of the product soluble in THF indicated formation of oligomers and polymer, with the largest fraction (78%) having a molecular weight of 0.6×10^3 (*vs.* PST) (PST = polystyrene), corresponding to the 4–5 mer, with 20% having a molecular weight of 0.8×10^3 (*vs.* PST), corresponding to the 6–7 mer, but with small peaks indicating higher molecular weight species of up to 2.5×10^3 (*vs.* PST). The results are similar to those for polymers obtained from UV light induced photodeposition performed using an excimer laser.[7]

Mass spectrometry measurements of the soluble polymer gave peaks at *m/z* 90; 155; 242; 289; 421; 460; 613; 766; 863; 919; 1073; 1190; 1340; 1425; 1495; 1574; 2129; 2518. MALDI experiments performed on the insoluble polymer showed masses peaking at about 1000 for PTCA and 1500 for PTBA. However MALDI may only be removing lower molecular weight fragments from the polymer mixture. The peaks were regularly spaced at intervals of 44, indicating that either carboxylate or boronic sidegroups were being removed under the conditions used to obtain the spectra.

The UV-vis spectrum (Fig. 1) of PTCA in DMF solution displays adsorption maxima at 425 and 585 nm, indicating that the polymer probably exists as a mixture of two species with different levels of conjugation, possibly different lengths of oligomers.[4] The UV spectrum of the solid form deposited on the inside of a polystyrene cuvette showed a different spectrum with higher absorption at longer wavelengths. These spectra and behaviour are very similar to that found in other polythiophenes with the spectra being dependent of the state of the polymer.[2,4,5]

FT-IR measurements of the product showed absorption bands specific to α-coupled polythiophene. IR (cm^{-1}): 3125, 1705, 1610, 1570, 1530, 1440, 1360, 940, 880, 840, 760, 710, 670, 630, 540. The broad peak between 3200–3700 cm^{-1} is characteristic for carboxylic OH absorption and the peak at 1705 characteristic of a carbonyl stretch. These results clearly confirm that the carboxylic

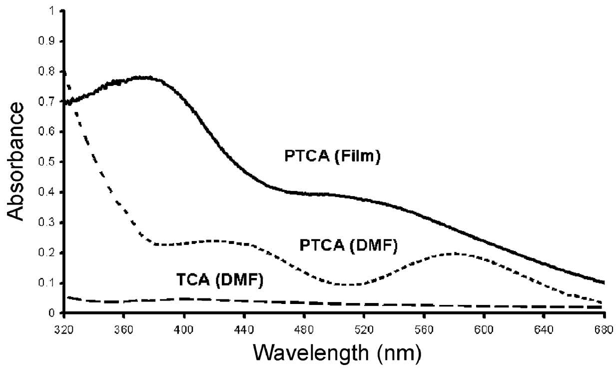

Fig. 1 UV-vis absorbance spectra of the PTCA and TCA solutions and films.

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† Electronic supplementary information (ESI) available: materials and spectroscopic methods used. See http://www.rsc.org/suppdata/cc/b4/b408387c/.

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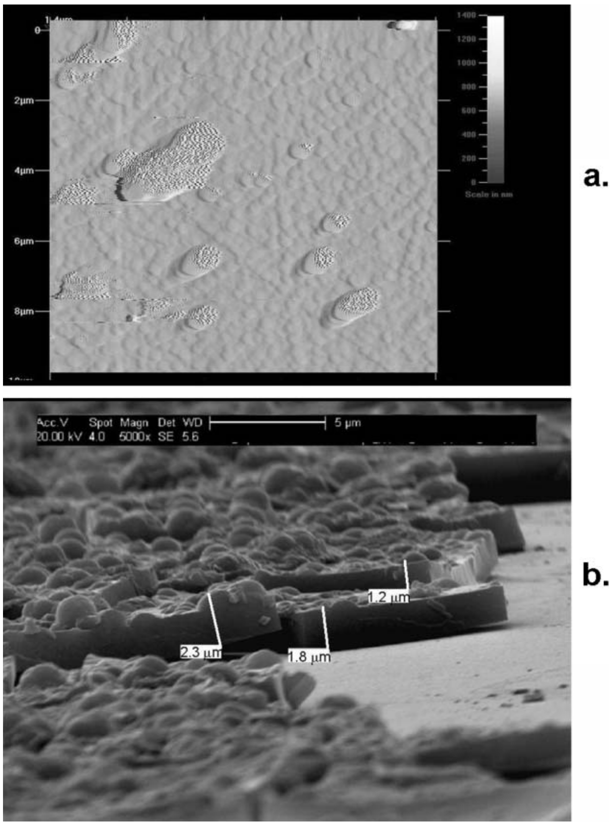


Fig. 2 (a) AFM of a photodeposited film of PTBA. (b) SEM cross-section of a photodeposited film of PTCA.

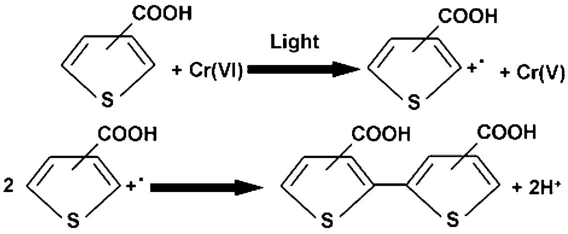
function withstood the applied oxidation conditions and remains in the resulting polymer. IR spectra of the monomers showed sharp peaks at about 3150 (TCA) and 3480 (TBA) corresponding to the C–H stretch; these were much reduced in the polymeric product, indicating loss of those bonds due to polymerization.

Ellipsometry studies and fitting of the data obtained showed that the PTCA film used for the UV measurements had a thickness of 0.59 μm with a roughness of 6.4 nm. The film had a refractive index of 1.63 at 800 nm, increasing gradually to 1.65 at 500 nm, 1.68 at 400 nm and 1.85 at 300 nm.

AFM and SEM studies were performed on films deposited onto polystyrene and show flat films with some granular structure (Fig. 2a). In an attempt to determine typical thicknesses, a film of PTCA was photodeposited onto a polycarbonate surface, the substrate was broken and analyzed using SEM; these images are shown in Fig. 2. The film shows a cracked appearance and the cross-section pictures (Fig. 2b) give a thickness of 1–2 μm.

Energy dispersive spectrography (EDS) analysis gave a surface composition indicating lower levels of Cr composition as compared to the soluble fraction (S : Cr atomic ratio of about 4 : 1).

A possible mechanism of the reaction is as follows. Due to the nucleophilic character of the –COOH group, 3-thiophenecarboxylic acid can not be polymerized using a traditional approach such as when $FeCl_3$ is used as oxidizing agent. In some cases polymerization of acidic derivatives was performed using a two step procedure involving first protection of the acid with benzyl group.[1] For the polymerization reaction to occur, three things must be present: monomer, dichromate ion and light. No reaction was observed when monomer and dichromate solutions were combined and stored in the dark and reaction was not seen to occur when potassium dichromate was replaced by other oxidants. Dichromate ion has been shown to be catalytically active in a series of photochemical reactions. A complex of Cr(VI)–TCA_3 was shown to catalyse the photopolymerization (440 nm) of methyl methacrylate in DMF.[10] No sign of complexation between $Cr_2O_7^{2-}$ and TCA, however, can be detected spectrophotometrically in the absence of illumination, which is in agreement with previous finding.[11] According to the suggested mechanism of photochemical polymerization (Scheme 1 showing dimer formation), the complex between monomer and Cr(VI), formed by complexation in the excited state, undergoes a charge-transfer reaction leading after a charge separation to Cr(V) and an organic radical.[11] This is followed by a spin-pairing of two radical cations to form a dihydrodimer dication, which subsequently undergoes a loss of protons and rearomatization.[6,10,12] Coupling occurs at the position of highest unpaired-electron spin density. The polymerization continues with the oxidation of the dimer[13] which undergoes further coupling reaction with other radical cations. The final photoproducts are Cr_2O_3 and poly-TCA.



Scheme 1 Mechanism of photopolymerisation.

In conclusion, we have demonstrated a novel polymerization method for α-linked oligo- and polythiophenes. The present photochemical polymerization method provides a basis for coating a surface with layers of new functional materials 0.5–2 μm thick and is potentially very useful for use in microelectronics and sensors.

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