polymer papers

Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between opaque blue-black and transparent sky blue

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The synthesis and properties of poly(3,4-ethylenedioxythiophene) (PEDOT) are reported. The polymer shows a low band-gap, 0.5 eV lower than that of polythiophene. This leads to very pronounced electrochromic properties since the doped polymer is almost transparent, with a sky-blue tint, and the neutral polymer is blue-black. The low band-gap also leads to the possibility of *n*-doping by electrochemical methods. The conductivity of the doped polymer is up to 200 S cm^{-1}, and the stability is remarkable, much better than observed in our studies of the polythiophene and polypyrrole families.

(Keywords: poly(3,4-ethylenedioxythiophene); synthesis; electrochromic properties)

INTRODUCTION

Conjugated organic polymers have attracted great attention because of their potential applications as electrical conductors, in electrochromic displays and smart windows, and in secondary batteries. These polymers, with a semiconductor-like band-gap in the blue-to-ultra-violet (u.v.) light range, can be oxidatively or reductively doped and turned into metal-like conductors. There is a strong interest in conjugated polymers with low band-gaps, because they could be intrinsically conducting without the necessity of doping. A general way to achieve low band-gaps is to synthesize fused ring aromatic or heteroaromatic monomers and obtain the low band-gap polymers from these monomers. Polyisothianaphthene[1] is the classic example of these, but examples of other fused rings are abundant. Another strategy has been the synthesis of donor–acceptor-type polymers. The most recent example is presented by Havinga, and has a band gap of 0.5 eV (ref. 2).

Conductive polymers with low band-gaps may also have favourable electro-optical properties. Ordinary conjugated polymers, studied for electrochromic displays and smart windows, usually have a band-gap in the violet or u.v. range (polyaniline, polypyrrole) or in the blue range (polythiophene). They are lightly coloured in the neutral state and become opaque or dark after doping. There are only a few polymers which are dark in the neutral state and become transparent after doping, for example polyisothianaphthene. However, low band-gap conjugated polymers with an absorption maximum in the middle of the visible range would behave in that way. After doping, the absorption maximum will shift to the near infra-red (n.i.r.) region, and the material becomes transparent in the visible (vis.) region. This is a desirable property for polymer electrochromic windows or displays. We have outlined how polymer electrodes can be combined with metal oxide counterelectrodes in solid-state polymer electrochromic devices[3], in such a manner as to use the metal oxide electrode as an optically passive electrode, and to rely exclusively on the optical changes in the polymer electrode for the colour change. In such a device, low band-gap polymers would be desirable.

It has been reported that alkoxy- and dialkoxythiophene polymers indeed show a band-gap lower than poly(alkylthiophene)[4–9], and that doped poly(cycloalkylenedioxythiophene)s are much more stable than poly(alkylthiophene)s and can function in humid and aqueous environments[10,11]. The alkoxy-substituted polythiophene will have a band-gap lower than non- and alkyl-substituted polythiophenes, owing to the presence of the two electron-donating oxygen atoms adjacent to the thiophene unit.

We therefore decided to synthesize the poly(cycloalkylenedioxythiophene)s. We found that poly(3,4-ethylenedioxythiophene) (PEDOT) has an optical absorption beginning at around 1.5 eV and reaching a maximum at around 2 eV, in the middle of the visible region. After doping, it becomes highly conducting with conductivity up to 200 S cm^{-1} (without optimization), and the absorption maximum appears at 0.6 eV, leaving the polymer almost transparent in the visible region. The material can be both hole- and electron-doped, and shows the best electrical stability we have ever observed in our studies of doped conjugated polymers.

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EXPERIMENTAL

The substituted thiophene monomer, 3,4-ethylenedioxythiophene (**7**) was synthesized following the early methods of Fager[12] and Guha and Iyer[13].

Thiodiglycolic acid (**1**, 50 g, Fluka) was dissolved in methanol (200 ml) and concentrated sulfuric acid (57 ml) was added slowly with continuous stirring. After refluxing for 16 h, the reaction mixture was cooled and poured into water (300 ml). The product was extracted with diethyl ether (200 ml) and the organic layer was repeatedly washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was distilled (172–176°C at 40 torr [1 torr = 133.3 Pa]) to give colourless dimethyl thiodiglycolate (**2**, 17 g).

A solution of **2** (17 g) and diethyl oxalate (**3**, 22 g) in methanol (100 ml) was added dropwise into a cooled (0°C) solution of sodium methoxide (34.5 g) in methanol (150 ml). After the addition was completed, the mixture was refluxed for 1 h. The yellow precipitate that formed was filtered, washed with methanol, and dried in vacuum at room temperature. A pale yellow powder of disodium 2,5-dicarbethoxy-3,4-dioxythiophene (**4**) was obtained in 100% yield (28 g).

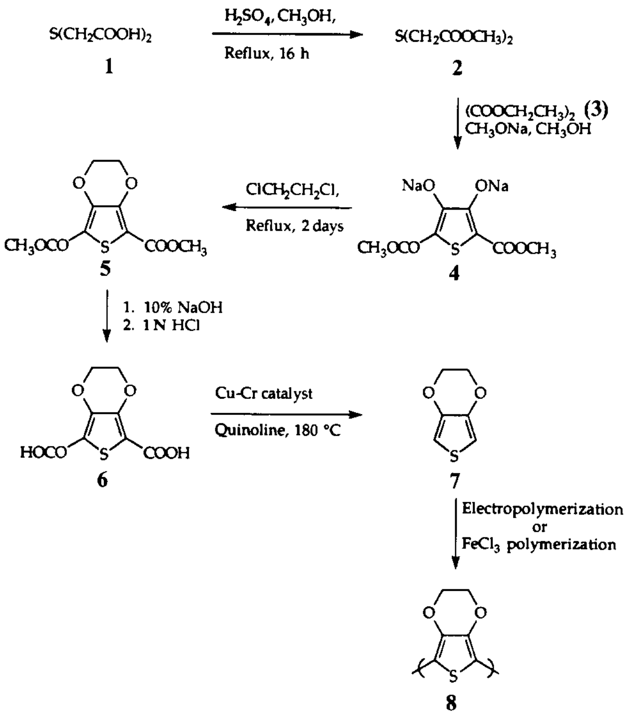
The salt (**4**, 2.5 g) was suspended in 1,2-dichloroethane (30 ml, Lab-Scan). After refluxing for 24 h, the mixture was cooled, and filtered to remove the unreacted starting material. Excess 1,2-dichloroethane was removed using a rotary evaporator. The residue, mainly 2,5-dicarbethoxy-3,4-ethylenedioxythiophene (**5**), was refluxed in 10 wt% aq. NaOH for 1 h. After cooling, the insoluble material was removed by filtration. Acidification of the filtrate led to a brown precipitate, which was recrystallized from methanol to give light-coloured needles of 2,5-dicarboxy-3,4-ethylenedioxythiophene (**6**, 0.6 g).

Barium-promoted copper chromite (0.2 g, Aldrich)[14] was added to the diacid (**6**, 0.5 g) in quinoline (5 ml) and the suspension was refluxed at 180°C under N_2 for 30 min. After cooling, diethyl ether was added and the insoluble catalyst removed by filtration. The filtrate was washed repeatedly with 1 M HCl, 1 M NaOH and water, and the ether was then removed using a rotary evaporator. The residue was purified by flash column chromatography (Silica gel 60, particle size 40–63 mm, toluene as eluent) to obtain 0.3 g of the monomer 3,4-ethylenedioxythiophene (**7**, EDOT, 0.3 g) in high yield (*Scheme 1*).

^1H n.m.r. (100 MHz, $CDCl_3$); δ (TMS) 6.20 (singlet, 2 H, 2 position of the thiophene ring), 3.89 (singlet, 4 H, ethylene hydrogens). ^{13}C n.m.r., (25 MHz, $CDCl_3$): δ (TMS) 141.2 (2C, 3 position of thiophene ring), 99.1 (2C, 2 position of thiophene ring), 64.0 (2C, ethylene carbons).

Chemical polymerization of **7** was achieved using anhydrous ferric chloride in acetonitrile. A black powder of poly(3,4-ethylenedioxythiophene) (**8**) was precipitated from the mixture. The black powder, probably the doped form of **8**, was insoluble in acetone, dimethylsulfoxide, *N*-methylpyrrolidone, methanol, acetic acid, acetonitrile, tetrahydrofuran, chloroform and water. It could be reduced to the neutral form using hydrazine in acetonitrile. The neutral product was not soluble in any of the solvents mentioned.

Electrochemical polymerization of **7** was conducted in a one-compartment, three-electrode cell, containing 0.05 M EDOT and 0.05 M tetraethylammonium perchlorate (Et_4NClO_4) in propylene carbonate (PC) or acetonitrile (ACN). We also used aqueous electrolytes, 0.01 M sodium polystyrenesulfonate, 0.05 M EDOT in water, for some electrochemical synthesis. A platinum wire counterelectrode and a Ag/AgCl reference electrode were used. The working electrode was either platinum-coated glass or indium–tin-oxide-coated glass of around 1 cm^2 area. For cyclic voltammetry, a platinum rod-tip was used as the working electrode. All experiments were conducted in laboratory air at room temperature.



Scheme 1

RESULTS

Since chemical polymerization using $FeCl_3$ produced a black material that was intractable, we concentrated on electropolymerization which produced a thin, transparent and rather homogeneous film on the working electrode. The as-prepared thin film was highly transparent with a light greenish-blue tint. The neutral film after electrochemical reduction was dark blue and less transparent than the doped one.

Electrochemical behaviour

A cyclic voltammogram (CV) of an EDOT solution is shown in *Figure 1*. The EDOT monomers are electro-oxidized and electropolymerized at potentials higher than 1.25 V *vs.* Ag/AgCl. The polymer deposited on the working electrode is electroactive and facilitates further electropolymerization, as shown in *Figure 2*.

Cyclic voltammetry of the polymer electrode was performed in contact with the electrolyte in the absence of EDOT. In *Figure 3* is shown the reversible redox of a PEDOT film in the potential range -1.0 to $+1.0$ V. At 100 $mV\,s^{-1}$ there are polymer oxidation peaks at -0.45 and $+0.25$ V and two deoxidation peaks at $+0.10$ and -0.55 V. The peak currents are linearly proportional to the scanning rate, indicating a surface-bound redox species.

CV scans in a wider potential range are shown in

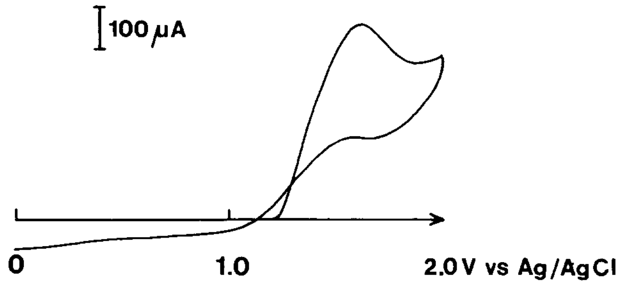


Figure 1 Cyclic voltammogram between 0.0 and 2.0 V *vs.* Ag/AgCl of 0.05 M EDOT in a 0.05 M Et_4NClO_4/acetonitrile solution. The working electrode was a Pt rod, and a Pt flag was the counterelectrode. The scan rate was $100 \, mV \, s^{-1}$. Onset of polymerization occurred at 1.25 V *vs.* Ag/AgCl

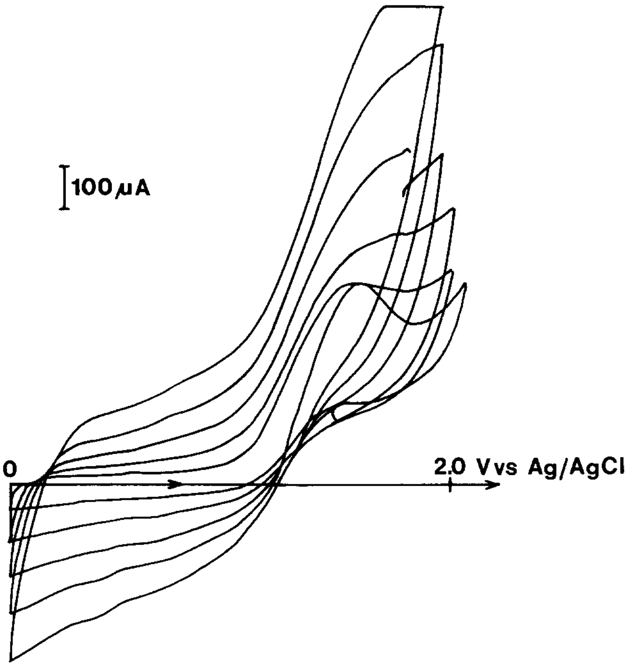


Figure 2 Continuous growth of PEDOT on a Pt rod. Same growth conditions as in *Figure 1*, but consecutive scanning

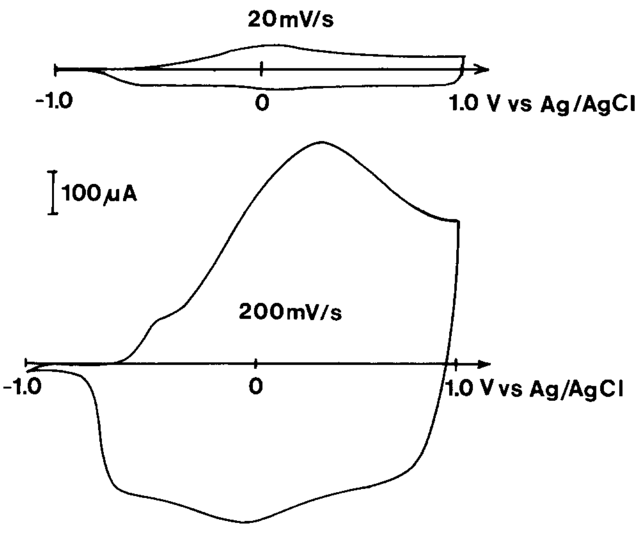


Figure 3 Cyclic voltammograms of a PEDOT film between −1.0 and +1.0 V *vs.* Ag/AgCl. The film was grown in the same medium as in *Figures 1* and *2* by the galvanostatic method, with a charge of 230 μA for 30 s = 6.9 mC, and characterized in the monomer-free electrolyte. The scan rates were between 20 and $200 \, mV \, s^{-1}$

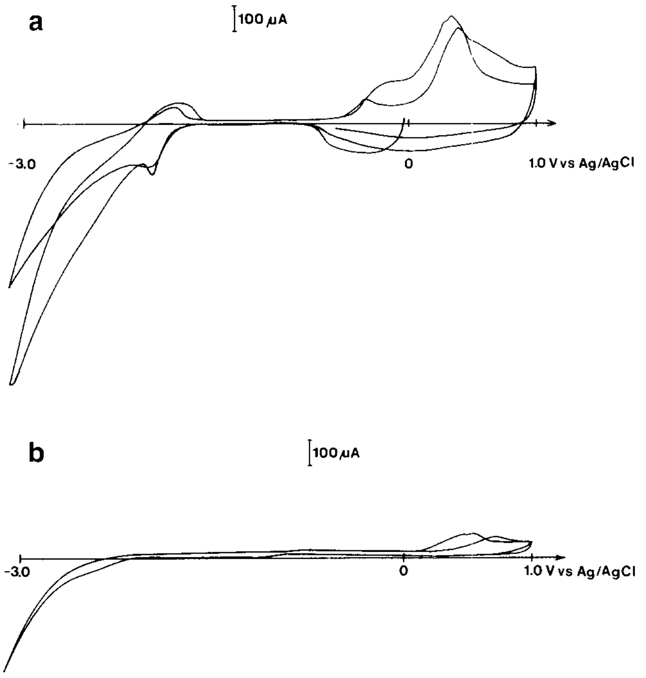


Figure 4 (a) A potential scan over a wider range (−3.0 to +1.0 V *vs.* Ag/AgCl) of a similar PEDOT film (also consuming 6.9 mC). No degradation of the electrolyte was observed in this range in a control experiment using a bare Pt rod electrode, as shown in the accompanying graph (b)

Figure 4. In addition to the oxidation–deoxidation redox peaks, there are a pair of reduction–dereduction peaks centred around −1.9 V *vs.* Ag/AgCl. This indicates that PEDOT can be not only oxidatively *p*-doped, but also reductively *n*-doped. The difference between the *p*-doping and *n*-doping onset potentials is around 1.5 V, close to the expected 1.5 V found by measuring the band-gap of this polymer as indicated by the onset of optical absorption.

Attempts at electropolymerization from PC or ACN solutions using either Et_4NOTs (tetraethyl ammonium tosylate) or TsOH (tosylic acid) as the supporting electrolyte were unsuccessful: only very thin PEDOT layers could be formed on the electrode. Also, adding even a trace amount of water to a Et_4NClO_4 solution in PC or ACN could kill the normal electropolymerization. We found, however, that PEDOT could be formed by electropolymerization from aqueous electrolytes, as reported previously[11].

Chemical and geometric structure

Our data do not allow any definite assignment of the chemical structure of PEDOT, because we still lack the elemental composition and i.r. data. We note, however, that the electrochemical polymerization of the EDOT proceeds in a smooth manner at a much lower potential than that of thiophene. We also note that the known competing polymerization patterns in thiophene, through the 3- and 4-position carbons, are blocked. There is therefore reason to believe that we have a mainly linear 2,5-coupling of EDOT. From the available data we cannot conclude what doping level is reached in the material. Earlier workers reported values from 30 to 40 mol%[11].

We have used X-ray diffraction to study whether any crystalline fraction is to be found in the doped PEDOT

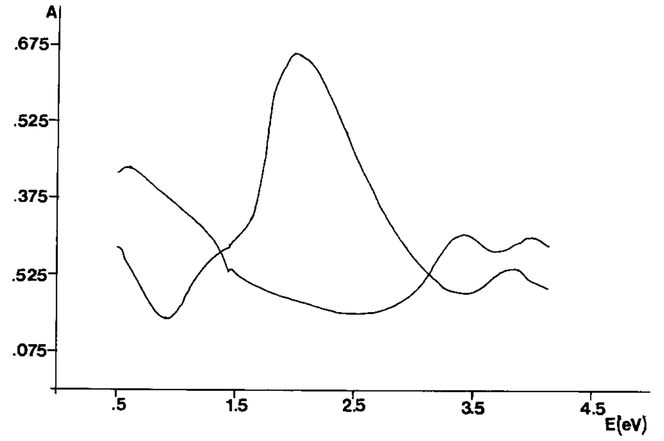


Figure 5 U.v./vis./n.i.r. absorption spectrum of a PEDOT film after reduction at -0.6 V *vs.* Ag/AgCl and after oxidation with $FeCl_3$ in ACN. This film was electropolymerized from an EDOT–Et_4NClO_4/PC solution at 1.5 V for 1 min, with 74 mC cm^{-2} of charge being consumed. The film was prepared on an ITO electrode

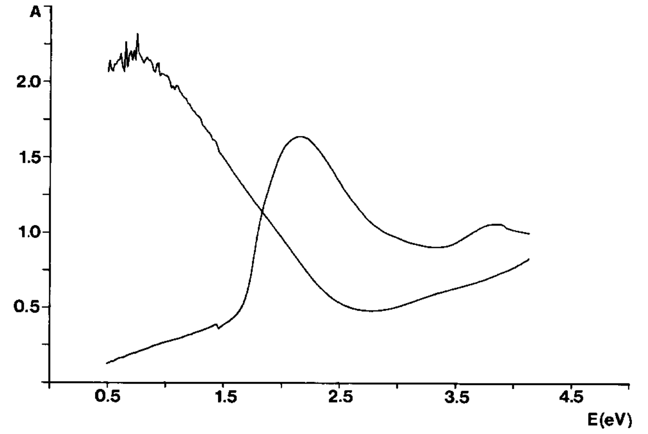


Figure 6 U.v./vis./n.i.r. spectra of dried PEDOT films as prepared from an EDOT–Et_4NClO_4/ACN solution at 1.5 V for 30 s ($Q = 100$ mC cm^{-2}) and dedoped at -1.0 V in a Et_4NClO_4/ACN solution free of EDOT. The film was deposited on an ITO electrode

with polystyrenesulfonate as counteranion, and found no crystallinity whatsoever. We conclude that the doped material is completely amorphous.

Optical absorption

Figure 5 shows the optical absorption spectra of PEDOT grown in PC in the neutral and chemically doped states. The neutral film shows a band-gap edge at around 1.5 eV and an absorption maximum at 2.0 eV, much lower than in polythiophene or poly(3-alkylthiophene). The doped film has a strong absorption in the n.i.r. range and is almost transparent in the vis. range. This transmission difference between the neutral and doped film in the vis. range is substantial, a feature essential for constructing smart windows.

After electrochemical growth of the polymer in ACN, we obtain the results reported in *Figure 6*. The as-prepared film is in the doped state with strong absorption in the n.i.r. region and high transparency in the vis. and u.v. regions, indicating the domination of bipolarons. The neutral film shows strong absorption in the vis. region with the maximum at 2.15 eV. The turn-on of optical absorption is found at 1.5 eV.

Figure 7 shows the *in situ* absorption spectra of a PEDOT film at various potentials in a Et_4NClO_4/ACN solution. The doped state shows typical bipolaron features, while the neutral one shows a rather broad absorption peak at 2.2 eV. Comparison to the spectrum in *Figure 5* may indicate that some solvatochromism may occur in PEDOT immersed in ACN.

Again, these spectra show the great absorption difference between the doped and neutral film. In fact, the neutral film has strong absorption just in the middle of the vis. region, that is, it is opaque to visible light. By contrast, the doped film shows the weakest absorption in this region. However, the absorption is still significant, possibly due to light scattering in the inhomogeneously doped sample, a feature which is common to almost all conjugated polymers after doping.

Conductivity

Thin, transparent, homogeneous PEDOT films were formed on Pt and ITO electrode surfaces from an EDOT–Et_4NClO_4/ACN solution by electropolymerizing at 1.3 V for 1 min, consuming 158 mC cm^{-2} of charge. These films were then removed from the electrode using double-sided adhesive tape. The as-prepared PEDOT films had shiny surfaces facing the electrode. The surface resistances were 50 Ω/square and the four-point probe conductivity was 210 S cm^{-1}. Since the experimental conditions have not been optimized, we expect to achieve even higher conductivity.

The neutral PEDOT film, after reduction at -1.0 V *vs.* Ag/AgCl in a solution of 0.05 M Et_4NClO_4 in ACN, is poorly conductive: conductivity is lower than 10^{-5} S cm^{-1}. The exact value remains to be determined (the film cracked upon drying, making a four-probe conductivity measurement impossible).

Stability

The stability of the perchlorate-doped, ~1 μm thick PEDOT film is extraordinarily high. *Table 1* lists the resistance of this film upon heating to 110 and 200°C in air. It is clear that little change occurs at 110°C; the decrease in resistance during the initial few minutes is due to thermal activation of the conductivity. Treatment at 200°C does induce large increases in resistance. Comparing this result to what we find with other

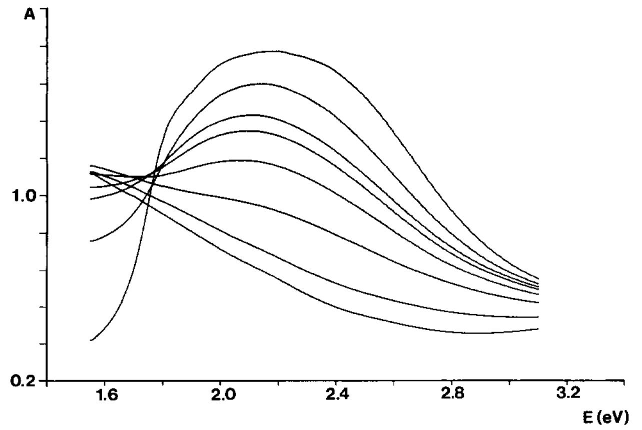


Figure 7 *In situ* absorption spectra of a potentiostatted PEDOT film at potentials between $+1.0$ V and -1.5 V *vs.* Ag/AgCl in a Et_4NClO_4/ACN solution. Comparison with the spectrum in *Figure 6* may indicate that some solvatochromism occurs in PEDOT immersed in ACN

Table 1 Stability of conductivity of doped PEDOT

Temperature (°C)	Time (min)	Resistance (Ω)
110	0	110
	2	107
	5.5	102
	43	78
	1200	78
	3810	79
200	0	57
	2	88
	8	100
	70	270
	1230	501
	3840	1260

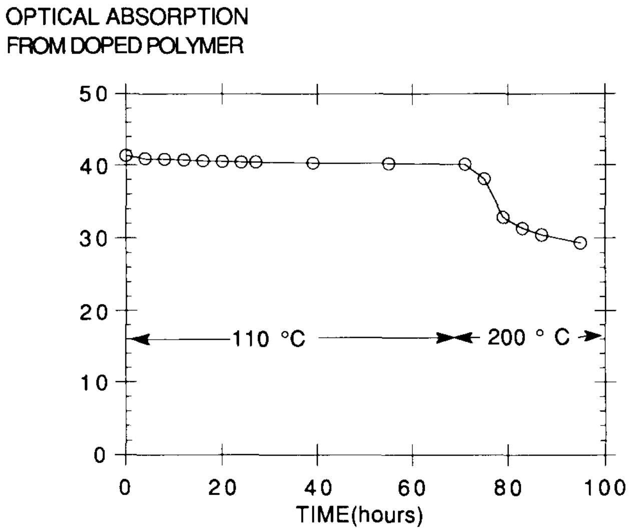


Figure 8 Stability of the optical spectrum of a doped PEDOT film undergoing thermal treatment in a light vacuum (10^{-2} torr [1.33 Pa]). The sample was grown at 1.3 V *vs.* Ag/AgCl in an aqueous electrolyte with 0.1 M sodium polystyrenesulfonate on an ITO electrode. The sample was mounted in the vacuum cell and the optical absorption was measured at regular intervals for 100 h. For the first 70 h the temperature was 110°C, thereafter it was increased to 200°C. The spectrum was evaluated by integrating the optical absorption between 0.5 and 0.9 eV, due to the doped form of the polymer, and plotting the optical absorption in this range *versus* time

substituted polythiophenes, it is outstanding. The poor stability of homopolymers of polyalkylthiophenes has been much improved with the random or regular copolymers of thiophene with sparsely decorated alkyl or alkyl phenylene side-chains, but also in these materials we find a complete loss of doping after 1200 min at 110°C[15–19]. The stability of PEDOT was also reported to be extremely high in earlier work on this material[10,11].

We have also studied the thermal stability of the doped polymer using optical spectroscopy. In this technique the sample is mounted inside a temperature-controlled vacuum cell of pressure 10^{-2} atm (1.3 Pa). Optical spectra are taken on the film at time intervals, and the decay of the conductivity can be correlated with the loss of absorption at the doping-induced peaks in the optical spectra. This technique was designed for the study of thermal undoping in poly(alkylthiophene)s[19]. We studied doped PEDOT films of a few thousand angstroms thickness at 110°C and found very little change ($\approx 2\%$) over 70 h. Therefore we raised the temperature to 200°C, where degradation accelerated strongly (see *Figure 8*).

CONCLUSIONS

The stability of doped PEDOT outperforms all earlier results on polymer stability in our laboratory, and demonstrates that conducting polymers stable in air are now available. The lack of processability, as well as the low yield of the monomer synthesis route, limits the attraction of the material. The stability is also crucial when it comes to applications in electrochemical systems, where a low rate of self-discharge would solve some of the current problems of polymer batteries. The rather low energy density, due to the heavy monomer, will limit the attraction of this material for use in secondary batteries.

The search for polymers for electrochromic windows, combining attractive optical properties with stability, is advanced with PEDOT. The low band-gap allows the polymer to be almost transparent in the doped state and blue-black in the neutral state. The presence of some optical absorption in the range 1.6–2 eV causes a film of the doped polymer to have a light sky-blue appearance; for better transparency it would be desirable to suppress the band-gap by another 0.2 eV. Studies of PEDOT in solid-state polymer electrochromic (smart) windows are in progress and the initial results are promising.

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