

SHORT COMMUNICATION

Poly(3-methylthiophenes) for an all polymer electrochromic device

C. ARBIZZANI, M. MASTRAGOSTINO, L. MENEGHELLO, M. MORSELLI, A. ZANELLI

University of Bologna, Department of Chemistry, 'G. Ciamician', via F. Selmi 2, 40126, Bologna, Italy

Received 9 March 1995; revised 22 May 1995

1. Introduction

It has been demonstrated that differences in the optical properties of 3-methylthiophene-based polymers make it possible to design a variable light transmission electrochromic device with two regiochemically and conformationally different polymers, poly(3-methylthiophene) and poly(3,3'-dimethyl-2,2'-bithiophene), operating in complementary mode in the visible region [1, 2].

The polymers electrosynthesized starting from 3-methylthiophene and 3,3'-dimethyl-2,2'-bithiophene show different optical properties owing to their different conjugation length. The maximum absorption of poly(3-methylthiophene) in the undoped form is at 530 nm and the polymer is purple and that of the undoped poly(3,3'-dimethyl-2,2'-bithiophene) is at 420 nm and the polymer is pale yellow; upon doping the colour of these polymers switches to pale blue and blue-violet respectively [3].

An important feature for electrochromic windows is an all-solid configuration and in this connection we present the performance of the poly(3-methylthiophene)/poly(3,3'-dimethyl-2,2'-bithiophene) electrochromic device with a polyacrylonitrile (PAN)-based gel electrolyte.

2. Experimental details

The poly (3-methylthiophene/PAN-electrolyte/poly(3,3'-dimethyl-2,2'-bithiophene) electrochromic device (2 cm² area) was assembled by sandwiching a doped poly(3-methylthiophene) and an undoped poly(3,3'-dimethyl-2,2'-bithiophene) counter-electrode with thickness of the order of 10⁻¹ μm, separated by a 100 μm Teflon spacer, and the PAN-based gel electrolyte.

The poly(3-methylthiophene) and poly(3,3'-dimethyl-2,2'-bithiophene) were galvanostatically grown on conductive glasses in nitrobenzene-tetrabutylammonium hexafluorophosphate 0.2 M, 3-methylthiophene 0.2 M at 5 mA cm⁻² and 5 °C with 50 mC cm⁻² and in acetonitrile-LiClO₄ 0.5 M, 3,3'-dimethyl-2,2'-bithiophene 0.01 M at 0.5 mA cm⁻² and 25 °C with 35 mC cm⁻², respectively. The polymer coverages were about 2.5 × 10⁻⁷ 3-methylthiophene unit moles cm⁻². The poly(3-methylthiophene) and poly(3,3'-dimethyl-2,2'-bithiophene) electrodes were conditioned in propylene carbonate (PC)-LiClO₄ 1 M by

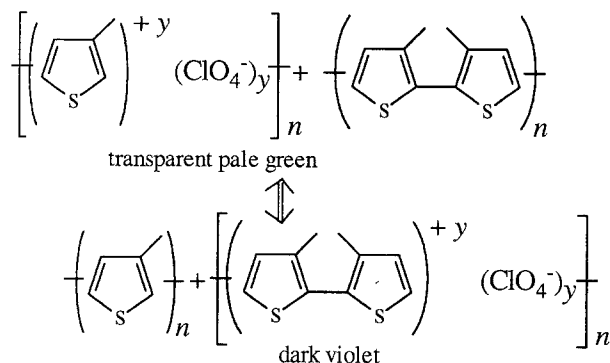
cyclic voltammetry from -0.5 to 1.0 V and 1.2 V vs SCE, respectively; the poly(3-methylthiophene) was potentiostatically charged at 0.9 V vs SCE in PC-LiClO₄ 1 M then washed in acetonitrile and dried before device assembling.

The gel electrolyte was prepared by mixing, at 70 °C, PAN, PC, ethylene carbonate and LiClO₄ in the weight ratios 10:42.5:42.5:5. Conductivity data were obtained by impedance measurements with stainless steel blocking electrode cells performed with a 1255 HF Solartron frequency response analyser and an M273 PAR potentiostat/galvanostat. The spectroelectrochemical measurements were carried out using AMEL electrochemical equipment and a Lambda 19 Perkin-Elmer spectrophotometer. All the chemicals were reagent-grade products purified before use.

3. Results and discussion

The PAN-based electrolyte is particularly suitable for electrochromic devices because of its transmittance (~100%) in the range 340-1800 nm, its high specific conductivity (Table 1) and its stability over long time (no conductivity loss has been observed at 25 °C over the entire test period, 2000 h).

By switching the applied voltage to the poly(3-methylthiophene)/ PAN-electrolyte/ poly(3,3'-dimethyl-2,2'-bithiophene) electrochromic device between 0.9 and -0.9 V (2-electrode mode), the resulting electrochemical process is



Scheme 1.

and the colour switches between transparent pale green and dark violet.

Figure 1 shows the optical spectra in the transparent and dark states of the device (the input of the conductive glasses supporting the electrochromic materials, which reduce transmittance regardless of the applied potential, has been subtracted because it

* Author to whom correspondence should be addressed.

Table 1. Conductivity data at different temperature of PAN-based gel electrolyte

$T/^\circ\text{C}$	-20	-10	0	10	20	25	30	40	50	60
$\sigma/\text{mS cm}^{-1}$	0.6	1.0	1.5	1.7	2.4	2.7	3.3	4.0	4.7	5.5

depends on the conductive glass type and on the manufacturer). The extent of light modulation in the entire visible region of this device is good and the electrochromic efficiency at $\lambda = 560 \text{ nm}$ (the wave-

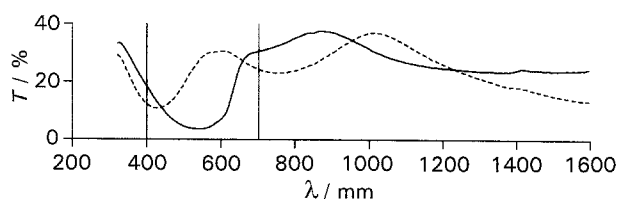


Fig. 1. Optical spectra of the poly(3-methylthiophene)/PAN-electrolyte/poly(3,3'-dimethyl-2,2'-bithiophene) device in the transparent ($\Delta V = 0.9 \text{ V}$, dashed line) and dark ($\Delta V = 0.9 \text{ V}$, solid line) states.

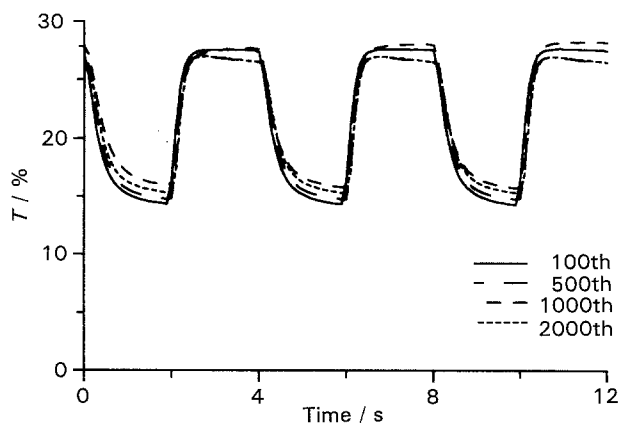


Fig. 2. Optical response of the poly(3-methylthiophene)/PAN-electrolyte/poly(3,3'-dimethyl-2,2'-bithiophene) device to repeated cycles starting from the 100th, 500th, 1,000th and 2,000th potential steps (4 s period) between 0.9 and -0.9 V , recorded at 560 nm .

length of maximum sensitivity of the human eye) is $0.25 \text{ mC}^{-1} \text{ cm}^2$, a high, advantageous value, especially for large area devices.

Figure 2 shows the device optical response to repeated potential switches between $+0.9$ and -0.9 V ; the response time is shorter than in the devices with inorganic ion-insertion counter-electrode materials and the stability to repeated switches is good. The optical memory is also satisfactory as the ratio between the transmitted light at λ several hours after the removal of the driving potential and that immediately after the removal is 0.96 in the transparent state over 16 h and 0.79 in the dark state over 3 h.

As smart windows for energy saving in buildings is the most important application of electrochromic devices, we evaluated how this device regulates the solar energy flux. The dotted line of Fig. 3 is the solar irradiance [4, 5] and the dashed and solid lines are the solar energy flux transmitted by the device in the bleached and dark state, respectively. Here, too, the input of the conductive glasses has been subtracted. The inset of Fig. 3 shows the partitioning of the transmitted energy flux in the three spectral regions. The first row of the histogram gives the percentage of the solar energy, and the others are the percentages of the transmitted energy in the ultraviolet, visible and near-infrared regions by the device in the pale green/dark violet colouring. This 3-methylthiophene-based device regulates only the visible light, the infrared remaining almost constant because, both in the bleached and in dark states, one polymer electrode is always in the doped form; for this reason the device

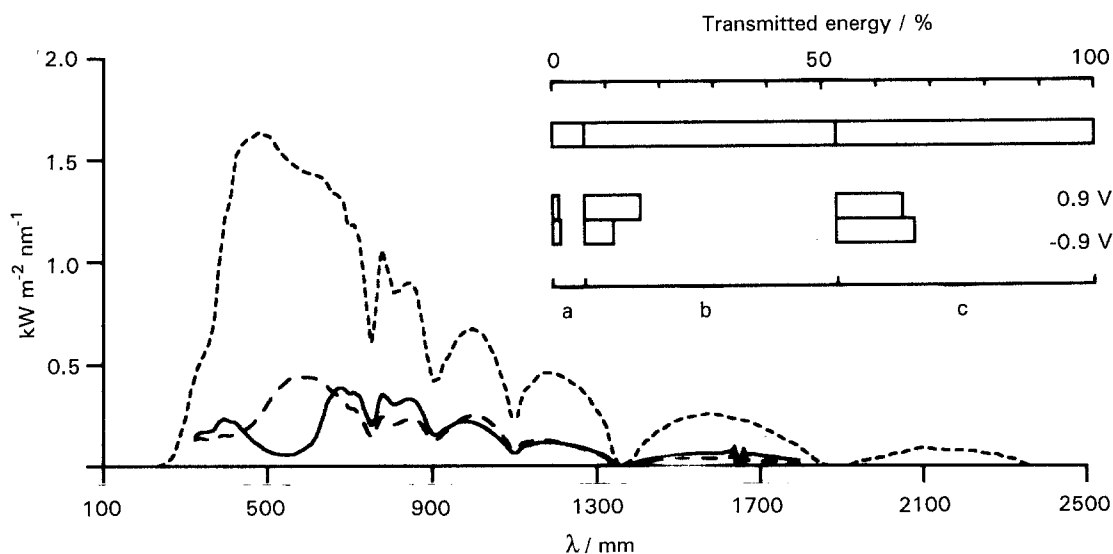


Fig. 3. Solar irradiance (dotted line) and transmitted solar energy flux by the poly(3-methylthiophene)/PAN-electrolyte/poly(3,3'-dimethyl-2,2'-bithiophene) device in the bleached (dashed line) and coloured (solid line) states. The histogram in the inset gives the percentage of the solar energy (first row) and percentages of the energy transmitted by the device in the 340–400 nm (a), 400–700 nm (b) and 700–1800 nm (c) spectral regions.

could be of some interest in tropical climates. All the figures show the performance of a device operating in a low transmittance range; however, increase in the device transmittance is easily achieved by decreasing the amount of electrochromic materials deposited on the glass electrodes and the electrochemical synthesis of the polymers is a convenient tool to control their thicknesses.

Acknowledgements

We wish to thank Dr G. Barbarella, I.Co.C.E.A., CNR, Ozzano (Bologna), Italy, who prepared the 3,3'-dimethyl-2,2'-bithiophene. The research

was funded by a grant of CNR, Progetto Finalizzato 'Materiali Speciali per Tecnologie Avanzate'.

References

- [1] C. Arbizzani, M. Mastragostino, L. Meneghello, X. Andrieu and T. Vicédo, *Mat. Res. Soc. Symp. Proc.* **293** (1993) 169.
- [2] C. Arbizzani, A. Bongini, M. Mastragostino, A. Zanelli, G. Barbarella and M. Zambianchi, *Adv. Mat.*, **7** (1995) 571.
- [3] C. Arbizzani, G. Barbarella, A. Bongini, M. Mastragostino and M. Zambianchi, *Synth. Metals* **52** (1992) 329.
- [4] B. P. Jelle, G. Hagen, *J. Electrochem. Soc.* **140** (1993) 3560
- [5] T. Ohta, 'Solar-Hydrogen Energy System', Pergamon Press, Oxford (1979).