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Solid state electrochemistry and spectroelectrochemistry of poly (arylene bisimide–alt-oligoether)s

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ABSTRACT

Two electroactive polymeric arylene bisimides, namely poly[(4,7,10-trioxatrideca-1,13-diyl)-(1,4,5,8-naphthalenetetracarboxylic bisimide-N,N′-diyl)] and its perylene analogue – poly[(4,7,10-trioxatrideca-1,13-diyl)-(3,4,9,10-perylenetetracarboxylic bisimide-N,N′-diyl)] have been synthesized and studied by cyclic voltammetry, UV–vis-NIR as well as Raman spectroeletrochemistry. Contrary to low molecular weight arylene bisimides, which show a clear two electron, double-step electrochemical reduction (neutral form to radical anion and from radical anion to dianion), in the synthesized polymers multielectron transfers are observed, accompanied with a strong electrochromic effect. However, as probed by cyclic voltammetry, their first reduction step is retarded and covers a wider potential range. We attribute this effect to macromolecular nature of the compounds being reduced and their structural inhomogeneity caused by π-stacking induced nanoaggregation of bisimide segments of the polymer chains. The second redox step seems unaffected by the polymeric nature of the electroactive compounds and yields a reduction peak similar to that registered for low molecular weight bisimides. Raman spectroelectrochemical data, combined with the established vibrational model of the perylene derivative – (poly[(4,7,10-trioxatrideca-1,13-diyl)-(3,4,9,10-perylenetetracarboxylic bisimide-N,N′-diyl)]) – enabled us to determine the mechanism of the first step of the electrochemical reduction process. The electrochemically induced shifts of the Raman bands unequivocally show that the reduction process results in the transformation of the carbonyl group into a radical anion. The surplus negative charge is delocalized on the six-member imide ring with the aromatic core very little affected.

1. Introduction

Low and high molecular weight aromatic bisimides are one of the most interesting organic semiconductors studied extensively in the past decade, especially in view of their application as active components of n-channel field effect transistors. This is caused by the possibility of precise tuning of their electronic properties either by core or by N functionalisation, combined with facile processing and air operating stability of some of these compounds [1,2]. Naphthalene and perylene bisimides with either alkyl- or ether-type substituents can be processed from solution in a form of thin films in which the crystallites are oriented in such a manner that the π-stacking direction is parallel to the substrate surface. This is of course advantageous from the technological point of view and allows the fabrication of transistors showing very good operating parameters [3,4]. Their high molecular analogues, *i.e.* polymers in which bisimide groups are linked either by alkylene or oligoether spacers, show a very poor field effect and cannot be used for the fabrication of high performance organic transistors [5]. This is caused by the fact that in this case it is difficult to achieve a supramolecular organization which would be favorable for charge carriers transport. Still polymeric arylene bisimides remain interesting and promising materials for several other technological applications since they are electroactive, electrochromic and luminescent (in the case of perylene derivatives). In this perspective, the determination of their solid state electrochemical and spectroelectrochemical properties is of crucial importance. In this communication we report on the synthesis and of two polymeric arylene bisimides, namely poly[(4,7,10-trioxatrideca-1,13-diyl)-(1,4,5,8-naphthalenetetracarboxylic bisimide-N,N′-diyl)] and its perylene analogue – poly[(4,7,10-trioxatrideca-1,13-diyl)-(3,4,9,10-perylenetetracarboxylic bisimide-N,N′-diyl)]. We concentrate on UV–vis and Raman spectorelectrochemistries since both methods are especially well suited for investigating thin polymeric film deposited on an electrode. The former technique provides valuable information on the electrochromism of elec-

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troactive polymers, whereas the latter one gives deep inside into the redox reaction mechanism. Great advantage of the use of Raman spectroelectrochemistry is based on the fact that this technique probes the changes in individual bond force constants of electrochemically active segments of the polymer studied. Since any charge transfer must result in a modification of the force constants, Raman spectroelectrochemistry is one of the most sensitive methods for the investigation of redox reaction mechanisms.

2. Experimental

2.1. Synthesis

2.1.1. Reagents and chemicals

Naphthalene 1,4,5,8-tetracarboxylic acid dianhydride, perylene 3,4,9,10-tetracarboxylic acid dianhydride, zinc acetate dihydrate, 4,7,9-trioxa-1,13-tridecadiamine and N-methylpyrrolidinone were purchased from Aldrich and used as received.

*2.1.2. Synthesis of poly[(4,7,10-trioxatrideca-1,13-diyl)-(1,4,5,8-naphthalenetetracarboxylic bisimide-N,N′-diyl)] (**1**)*

1 g of naphthalene 1,4,5,8-tetracarboxylic acid dianhydride (3.73 mmol), 0.819 g of zinc acetate dihydrate (3.73 mmol) and 0.821 g of 4,7,9-trioxa-1,13-tridecadiamine (3.73 mmol) were stirred in 30 ml of N-methylpyrrolidinone for 0.5 h in 120 °C and 2.5 h in 180 °C. Complete consumption of dianhydride was confirmed by IR spectroscopy. The reaction mixture was cooled and poured onto 120 ml of methanol. The obtained precipitate was filtered off and washed with methanol. Obtained light beige solid was vigorously stirred with acetone for 12 h to remove remaining impurities and filtered off again to yield 1.422 g (84%) of product. The solid was partitioned into fractions soluble and insoluble in chloroform using a Soxhlet apparatus. The soluble fraction after drying at 60 °C for 2 h weighted 0.704 g (41.7%).

^1H NMR (400 MHz, $CDCl_3$ + 1 drop of CF_3COOD): δ = 8.64–8.72 (broad, 4H), 4.20–4.30 (broad, 4H), 3.62–3.74 (broad, 12H), 1.98–2.10 (broad, 4H).

^{13}C NMR (100 MHz, $CDCl_3 + CF_3COOD$ 5:1): δ = 163.2 (C=O), 131.3, 126.3, 125.8, 69.9, 69.6, 69.1, 38.4, 27.5.

IR (KBr, cm^{-1}): 3081, 2921, 2866, 1704, 1662, 1581, 1455, 1376, 1341, 1243, 1184, 1116, 971, 879, 769.

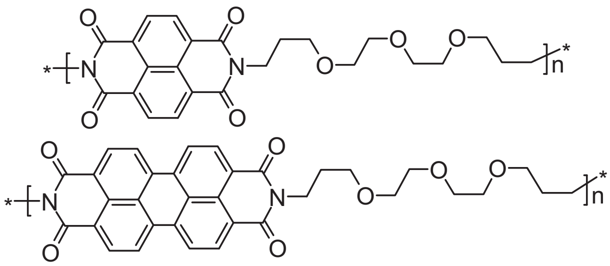
UV–vis ($CHCl_3$, nm): 381, 360, 343.

Elemental analysis: calcd. C 63.71, H 5.35, N 6.19; found C 63.57, H 5.35, N 6.06.

$M_n = 2530$, $M_w = 7190$, $D = 2.84$.

*2.1.3. Synthesis of poly[(4,7,10-trioxatrideca-1,13-diyl)-(3,4,9,10-perylenetetracarboxylic bisimide-N,N′-diyl)] (**2**)*

1 g of perylene 3,4,9,10-tetracarboxylic acid dianhydride (2.55 mmol), 0.560 g of zinc acetate dihydrate (2.55 mmol) and 0.562 g of 4,7,9-trioxa-1,13-tridecadiamine (2.55 mmol) were stirred in 30 ml of N-methylpyrrolidinone for 0.5 h in 120 °C and 1.5 h in 180 °C and 1 h in 190 °C. Complete consumption of dianhydride was confirmed by IR spectroscopy. The reaction mixture was cooled and poured onto 120 ml of methanol. The dark red precipitate was filtered off and washed with methanol. Obtained brown-red solid was vigorously stirred with acetone for 12 h to remove remaining impurities and filtered off again to yield 1.235 g (84%) of dark red powder. Using a Soxhlet apparatus the solid was partitioned into two fractions: one insoluble in chloroform (dark red-brown powder) and a second fraction (black crystalline-like powder) which formed a colloidal suspension in this solvent. The colloidal fraction after drying at 80 °C for 6 h weighted 0.198 g. It could be solubilized by addition of trifluoroacetic as a co-solvent.



1

2

Chart 1. Chemical formulae of poly[(4,7,10-trioxatrideca-1,13-diyl)-(1,4,5,8-naphthalenetetracarboxylic bisimide-N,N′-diyl)] (**1**) and poly[(4,7,10-trioxatrideca-1,13-diyl)-(3,4,9,10-perylenetetracarboxylic bisimide-N,N′-diyl)] (**2**).

^1H NMR (400 MHz, $CDCl_3 + CF_3COOD$ 3:1): δ = 8.20–8.60 (broad, 8H), 4.28–4.40 (broad, 4H), 3.80–4.04 (broad, 12H), 2.15–2.22 (broad, 4H).

IR (KBr, cm^{-1}): 3093, 2921, 2858, 1694, 1653, 1593, 1577, 1441, 1403, 1343, 1243, 1175, 1009, 1082, 962, 852, 809, 793, 744.

UV–vis ($CHCl_3$, nm): 529, 492, 462.

Elemental analysis: calcd. C 70.82, H 4.89, N 4.86; found C 67.71, H 5.12, N 4.60.

2.2. Characterisation techniques

Solution spectra of the of the obtained polymers, dissolved in chloroform and solid state spectra of their thin films deposited on an ITO electrode were recorded on a Varian Cary 5000, likewise the Infrared spectra were recorded using either a Perkin Elmer (System 2000) spectrometer or on a Cary 2300 double beam spectrophotometer.

Chronovoltamperometric studies were carried out for the solutions of **1** and for thin solid films of both polymers (**1** and **2**). In the first case 2.5×10^{-4} mol dm^{-3} solution of **1** in 0.1 mol dm^{-3} Bu_4NBF_4/CH_2Cl_2 electrolyte was placed in a one-compartment, three electrode electrochemical cell with a platinum working electrode of the surface area of 3 mm^2, a platinum mesh counter electrode and an Ag/0.1 mol dm^{-3} Ag^+/acetonitrile reference electrode. The measurements were performed using an Autolab potentiostat (Eco Chemie). The potential of the reference *vs* Fc/Fc^+ redox couple was checked at the end of each experiment. In the second case thin films of **1** and **2** were deposited on a platinum electrode by casting. The measurements were carried out in 0.1 mol dm^{-3} Bu_4NBF_4/CH_3CN electrolyte, in the same electrochemical cell and using the same set of working, counter and reference electrodes.

For UV–vis-NIR and Raman spectroelectrochemical investigations thin layers of 1 and 2 were deposited by casting on an ITO electrode and a Pt electrode, respectively. In the measurements the same counter (Pt) and reference (Ag/Ag^+) electrodes, and the same electrolyte (0.1 mol dm^{-3} Bu_4NBF_4/CH_3CN) as in the case of chronovoltamperometric studies were used. Both Raman and UV–vis electrochemical cells were of rectangular shape (30 mm × 14 mm × 6 mm). All the three electrodes were in close vicinity, so the iR drop was negligible. The potential of the reference electrode was verified using the ferrocene couple at the end of each set of spectroelectrochemical investigations. The UV–vis-NIR spectra were recorded on a Varian Cary 5000 spectrometer whereas the Raman spectra – on a FT Raman Brucker RFS 100 spectrometer with the near-IR excitation line (1064 nm).

3. Results and discussion

Both polymers synthesized in this research are depicted in Chart 1.