RSC Advances

PAPER

Cite this: *RSC Adv.*, 2015, **5**, 93591

Synthesis and characterization of novel electrochromic poly(amide-imide)s with *N*,*N*′-di(4-methoxyphenyl)-*N*,*N*′-diphenyl-*p*-phenylenediamine units†

Sheng-Huei Hsiao,*[a] Chia-Yin Teng[a] and Yu-Ruei Kung[b]

We developed a new efficient procedure for the synthesis of a bistriphenylamine diamine monomer, *N*,*N*′-bis(4-aminophenyl)-*N*,*N*′-bis(4-methoxyphenyl)-1,4-phenylenediamine (**3**). A new dicarboxylic acid monomer bearing two built-in imide rings, namely *N*,*N*′-bis(trimellitimidophenyl)-*N*,*N*′-bis(4-methoxyphenyl)-1,4-phenylenediamine (**4**), was synthesized from the condensation of diamine **3** with two equivalent amounts of trimellitic anhydride. Several novel electroactive poly(amide-imide)s (PAIs) containing *N*,*N*′-di(4-methoxyphenyl)-*N*,*N*′-diphenyl-*p*-phenylenediamine [TPPA(OMe)$_2$] units have been prepared by the phosphorylation polyamidation reactions from diamine **3** with four imide ring-preformed dicarboxylic acids or from diimide-diacid **4** with 4,4′-oxydianiline and diamine **3**, respectively. All the PAIs were readily soluble in many organic solvents and could be solution-cast into tough and flexible polymer films. These PAIs exhibited glass-transition temperatures (T_gs) in the range 206–292 °C, and most of them did not show significant weight-loss before 450 °C. The PAI films revealed reversible electrochemical oxidation processes accompanied with strong color changes from the pale yellow neutral state to yellowish green and deep blue oxidized. Incorporating the TPPA(OMe)$_2$ unit on the amide side of PAIs led to lower oxidation potentials and higher redox and electrochromic stability.

Received 29th August 2015
Accepted 25th October 2015

DOI: 10.1039/c5ra17520h

www.rsc.org/advances

1. Introduction

Electrochromism is defined as a reversible change in optical absorption (or transmittance) and color change resulting from the redox of the material in response to an externally applied potential by electrochemical means which has stimulated the interest of scientists over the past few decades.[1] Traditionally, interest in electrochromic materials has been directed towards optical changes in the visible region, leading to many technological applications such as variable reflectance mirrors, smart windows, and electrochromic displays.[2–4] One of the main use of electrochromic materials is in smart windows for car and buildings[5] and in automatic-dimming rear-view mirrors.[6] Recent high-profile commercialization of electrochromic materials includes the Boeing 787 Dreamliner windows manufactured by Gentex.[7] Potential applications in information storage,[8] electrochromic displays,[9] and adaptive camouflages[10] can also be envisioned. There are several chemical systems that are intrinsically electrochromic, such as transition metal oxides (especially tungsten oxide), inorganic coordination complexes, small organic molecules, and conjugated polymers (polyanilines, polypyrroles, and polythiophenes).[1–4] Electrochromic applications based on π-conjugated polymers become popular owing to their ease of colour-tuning, fast switching time, and high contrast ratios.[11–15] Studies from the Reynolds research group have shown a wide variety of conjugated polymers with colour changes that cover the entire visible spectrum.[16–20]

Triarylamine derivatives are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.[21–23] During the last decade, Liou's and our research groups have developed a number of high-performance polymers, such as aromatic polyamides and polyimides, carrying the triarylamine unit as an electrochromic functional moiety.[24–32] Our strategy was to synthesize the triarylamine-containing monomers such as diamines and dicarboxylic acids that were then reacted with the corresponding co-monomers through conventional polycondensation techniques. The obtained polymers possessed characteristically well-defined structures, high molecular weights, and high thermal stability. Because of the incorporation of packing-disruptive, propeller-shaped triarylamine units along the polymer backbone, almost all the polyamides and some of the polyimides exhibited good solubility in polar organic solvents. They could form uniform, transparent

[a]*Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan. E-mail: shhsiao@ntut.edu.tw*

[b]*Div. of Organic Opto-electronic Materials and Applications, Material and Chemical Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra17520h