European Polymer Journal 73 (2015) 50–64

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Synthesis and electro-optical properties of aromatic polyamides and polyimides bearing pendent 3,6-dimethoxycarbazole units

Sheng-Huei Hsiao [a,*], Siao-Chi Peng [a], Yu-Ruei Kung [b], Chyi-Ming Leu [b], Tzong-Ming Lee [b]

[a] *Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan*
[b] *Div. of Organic Opto-electronic Materials and Applications, Material and Chemical Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan*

ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form 20 September 2015
Accepted 6 October 2015
Available online 8 October 2015

Keywords:
Polyamides
Polyimides
Carbazole
Electrochemistry
Electrochromism

ABSTRACT

This work deals with the synthesis and characterization of a new *m*-phenylenediamine-type monomer with pendent 3,6-dimethoxycarbazole group, namely *N*-(4-(3,6-dimethoxy carbazol-9-yl)phenyl)-3,5-diaminobenzamide (**2**), and its derived aromatic polyamides and polyimides. New electroactive aromatic polyamides were synthesized from diamine **2** with four aromatic dicarboxylic acids via the phosphorylation polyamidation technique, and the polyimides were prepared from equimolar mixtures of 4,4′-oxydianiline and diamine **2** with four aromatic tetracarboxylic dianhydrides via a conventional two-step procedure. All the polyamides and the 6FDA-derived polyimide were readily soluble in many organic solvents and could afford strong and flexible films by solution casting. The polymers showed useful levels of thermal stability with glass-transition temperatures (T_gs) in the range of 237–313 °C and 10% weight-loss temperatures in excess of 450 °C. All the polyamides and polyimides showed reversible electrochemical oxidation, accompanied by strong color changes. By incorporation of electron-donating methoxy groups on the electrochemically active C-3 and C-6 sites of the carbazole unit, the polymers exhibit greatly enhanced electrochemical stability and electrochromic performance in comparison with the analogs without any substituents on the carbazole unit.

1. Introduction

Aromatic polyaimdes and polyimides are well accepted as high-performance polymers because of their good thermal and chemical stability, excellent mechanical properties, and high glass transition temperatures [1–4], and are widely used in various fields including aerospace and electronic industries. However, these polymers are difficult to process due to their high glass transition temperatures (T_g), or high melting temperatures (T_m), and limited solubility in organic solvents. Considerable efforts have been made to improve the solubility and melting processability of polymers while maintaining their positive properties [5–7]. A variety of structural modifications to the polymer backbone, such as insertion of flexible linkage on main chain and utilization of noncoplanar or asymmetric monomers, incorporation of pendent groups in the polymer backbone, can be used to modify the polymer properties, either by lowering the inter-chain interaction or by reducing the stiffness of the polymer chain. Depending on the type and amount of structural modification, the melting temperatures can be lowered and the solubility improved, resulting in processable materials [8–15].

---

[*] Corresponding author.
E-mail address: shhsiao@ntut.edu.tw (S.-H. Hsiao).

http://dx.doi.org/10.1016/j.eurpolymj.2015.10.004

Carbazole are well-known hole-transporting and light-emitting units. Carbazole can be easily functionalized at the (3,6)-, (2,7)-, or *N*-positions and then covalently linked into polymeric systems, both in the main chain as building blocks and in the side chain as pendent groups [16]. Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various optoelectronic applications such as photoconductive, electroluminescent, electrochromic, and photorefractive materials [17–19]. As reported previously [20–22], carbazole group can be used as a fluorophore and electrochromophore onto the backbones of high-performance polymers such as aromatic polyamides and polyimides. However, the electrogenerated cation radical of carbazole is not reversible, possibly due to the electrochemical coupling of carbazoles through the active C-3 and C-6 sites [23]. This may lead to problems with electrochemical and electrochromic stability of this kind of electrochromic materials. It has been demonstrated that introduction of bulky groups such as *tert*-butyl group on the electrochemically active sites (C-3 and C-6) of carbazole leads to enhanced electrochemical and morphological stability [24–27]. Very recently, we have illustrated that carbazole containing polyamides and polyimides exhibited even lower oxidation potentials and higher electrochemical stability if the electrochemically active sites (C-3 and C-6) of carbazole were protected with the electron-donating methoxy group [28,29]. In a effort to continue our work in the design and synthesis of carbazole-based electrochromic polymers with better performance, in this work an aromatic diamine monomer with pendent 3,6-dimethoxycarbazol-9-yl group, namely *N*-(4-(3,6-dimethoxycarbazol-9-yl)phenyl)-3,5-diaminobenzamide (Compound **2** in Scheme 2), was synthesized and led to serial aromatic polyamides and polyimides. Basic characterizations, electrochemical and electrochromic properties of the polymers were studied. The effect of the incorporation of methoxy group on the C-3 and C-6 positions of pendent carbazole units on the properties of these polymers was also investigated.

2. Experimental section

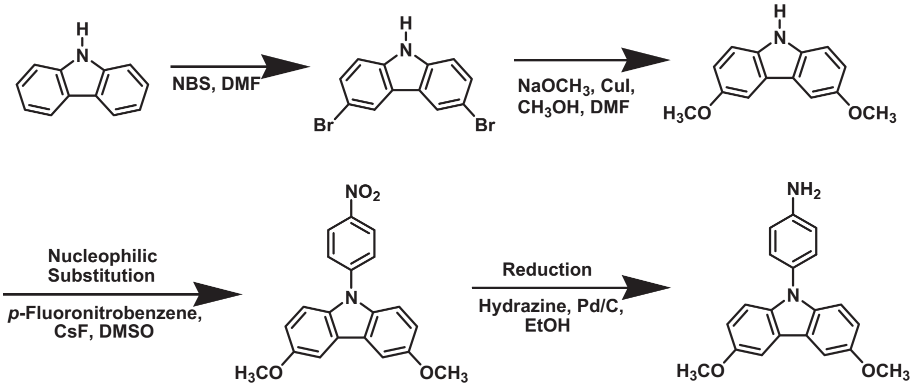
2.1. Materials

Carbazole (Acros), *p*-fluornitrobenzene (Acros), cesium fluoride (CsF) (Acros), 10% palladium on charcoal (Pd/C, Acros), 3,5-dinitrobenzoyl chloride (Arcos), triethylamine (Acros), triphenyl phosphite (TPP, Acros), and 80% hydrazine monohydrate (TCI) were used without further purification. *N*,*N*-Dimethylacetamide (DMAc, Acros) and *N*-methyl-2-pyrrolidone (NMP, Acros) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. The aromatic dicarboxylic acid monomers such as 4,4′-biphenydicarboxylic acid (**3a**) (TCI), 4,4′-dicarboxydiphenyl ether (**3b**) (TCI), bis(4-carboxyphenyl) sulfone (**3c**, Acros), and 2,2-bis(4-carboxyphenyl)hexafluoropropane (**3d**, TCI) were used as received from commercial sources. The aromatic tetracarboxylic dianhydrides including 3,3′4,4′-biphenyltetracarboxylic dianhydride (**5a**, BPDA) (Oxychem), 4,4′-oxydiphthalic dianhydride (**5b**, ODPA) (Oxychem), 3,3′4,4′-diphenylsulfonetetrscarboxylic dianhydride (**5c**, DSDA) (Oxychem) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**5d**, 6FDA) (Hoechst Celanese) were purified by dehydration at 250 °C in vacuo for 3 h. Commercially obtained calcium chloride was dried under vacuum at 150 °C for 6 h prior to use. Tetrabutylammonium perchlorate (Bu_4NClO_4) (Arcos) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried in vacuo. All other reagents and solvents were used as received from commercial sources. As depicted in Scheme 1, the 3,6-dimethoxy-*N*-(4-aminophenyl)carbazole was synthesized according to a four-step synthetic route reported in a previous article [27].

2.2. Monomer synthesis

2.2.1. N-[4-(3,6-Dimethoxycarbazol-9-yl)phenyl]-3,5-dinitrobenzamide (1)

In a 250 mL round-bottom flask equipped with a stirring bar and a nitrogen gas inlet tube, 3.18 g (0.01 mol) of 3,6-dimethoxy-9-(4-aminophenyl)carbazole were dissolved in 20 mL of DMF and 1.01 g (0.01 mol) of trimethylamine was added into



Scheme 1. Synthetic route to 3,6-dimethoxy-9-(4-aminophenyl)carbazole.