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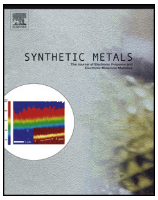

Photophysical, electrochemical and thermal properties of new (co)polyimides incorporating oxadiazole moieties

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ABSTRACT

New polyimides and copolyimides were obtained by polycondensation of 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole with one of the three aromatic dianhydrides: 1,4,5,8-naphthalenetetracarboxylic dianhydride, 4,4′-(4,4′-isopropylidene-diphenoxy)bis(phthalic anhydride) and 4,4′-tetraphthaloyl-bis(1,8-naphthalene dicarboxylic)dianhydride. The photophysical properties such as UV absorption, photoluminescence (PL), electrochemical and spectroelectrochemical properties of the copolymers were evaluated. Additionally, their thermal behavior was investigated. The polymers dissolved in NMP and in the solid state as blend with nonemissive poly(methyl methacrylate) emitted blue light with the highest intensity under excitation wavelength (λ_{ex}) 340 nm, whereas, under λ_{ex} = 405 nm green fluorescence was observed with double-exponential lifetime. Longer decay constants were estimated for polymers in blend as compared with the ones obtained for solutions. The electronic properties, such as, HOMO–LUMO levels and band gaps were calculated via cyclic voltammetry (CV) and differential pulse voltammetry (DPV) and for models of polyimides were calculated theoretically by density functional theory (DFT). All of the polymers exhibited reversible reduction and non-reversible oxidation process. The electrochemical band gaps based on DPV measurements were in the range of 1.79–2.50 eV. Spectral changes in UV–vis region under applied potential were observed. Decreasing of applied potential to negative values resulted in appearance of new band around 600 nm in the case of film prepared from polyimide with naphthalene diimide rings and with copolyimide containing naphthalene diimide and phthalic imide structures. The obtained polymers exhibited glass transition temperatures (T_g) in the range of 227–336 °C and decomposition temperature (T_d) in the range of 382–505 °C.

1. Introduction

Since the first produced aromatic polyimides (PIs) in 1908 interest in this class of polymers has been growing steadily because of their outstanding properties such as thermo-oxidative stability, unique electrical properties, high radiation and solvent resistance, and high mechanical strength [1]. Recently they have received attention due to their tendency to form n-type organic semiconductors [2]. The excellent combination of properties makes them suitable for a wide range of applications. PIs have been adopted as insulating or dielectric materials, photoresists, liquid crystal alignment layers, gas separation membranes, composites and LB films. They have also been investigated for applications in advanced technologies as photovoltaics, fuel cells, electrochromic, photochromic, electroluminescent, xerography, nonlinear optical, polymer memory materials and nanomaterials [1,3–8].

Oxadiazole-based polymers possess a combination of properties such as thermal and chemical stability, strength, stiffness, that makes them good candidates for various applications as high temperature fibers, reinforced materials and membranes for gas separation [9]. Particularly interesting are properties determined by their electronic structure because they are characterized by high electron affinity. The electronic properties combined with their high heat resistance made them attractive for applications in microelectronics, optoelectronics, advanced telecommunications or other related fields. Their electron-withdrawing character facilitates the injection and transport of electrons and both low molecular weight compounds and polymers with oxadiazole structure have been shown to be promising electron-transporting materials in light-emitting and electronic memory devices

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[4,10–12]. However, it was found that the oxadiazole units can also act as electron donors when they are bonded to stronger electron acceptors such as phthalimide moieties [4]. Thus, polyimides with oxadiazole units create donor–acceptor (D–A) system which is desirable for organic optoelectronic and electronic applications, including electroluminescent materials for polymeric or organic light emitting devices (PLEDs and OLEDs), photovoltaic devices, electrochromic devices, field-effect transistors (FETs), polymer memory materials, and other photoelectronic devices [4,13]. Oxadiazole units may be introduced into polyimides by two methods. In the first, and the most common one, PIs with oxadiazole moieties are prepared from oxadiazole-containing diamines. Another approach is the cyclodehydration at elevated temperatures of the poly(hydrazide-imide) [14–16]. Poly(oxadiazole-imide)s or their precursors, that is, poly(hydrazide-imide)s are usually prepared by polycondensation carried out in solvent, however, they can be also synthesized by vapor deposition polymerization [17].

The literature survey showed that oxadiazole-containing PIs have been described from the point of view of potential applications in advanced optoelectronics. However, polymers presented in this work are new except for one which was described in our previous work [18]. Short literature review below is devoted to the oxadiazole based polyimides in which their luminescence and/or electronic properties have been reported. Hsu et al. [17] reported electroluminescence and electrochemical properties of polyimide film prepared from 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole (BAO) polycondensed with 4,4-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) by vapor deposition polymerization. The emissive peak of film was located at 550 nm. The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was −6.51 eV and −3.32 eV referred to the vacuum level, respectively. Hamciuc et al. described poly(1,3,4-oxadiazole-ether-imide)s [19] and poly(1,3,4-oxadiazole-imide)s [20] synthesized by polycondensation reaction of BAO, 2,5-bis[p-(4-aminophenoxy)phenyl]-1,3,4-oxadiazole (BAOXD), 2,5-bis[p-(3-aminophenoxy)phenyl]-1,3,4-oxadiazole (m-BAOXD), 2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole and 2-(4-fluorophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole with 1,1,1,3,3,3-hexafluoro-2,2-bis-[(3,4-dicarboxyphenoxy)phenyl] propane dianhydride and with bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride, respectively. Fluorinated poly(1,3,4-oxadiazole-ether-imide)s showed maximum emission wavelength (λ_{em}) was in the range of 372–424 nm in DMF solution [19]. Whereas, poly(1,3,4-oxadiazole-imide)s containing dimethylsilane exhibited photoluminescence (PL) in DMF solution with λ_{em} from 353 nm to 428 nm [20]. BAOXD was reacted with 6FDA and resulted PI was examined as potential memory devices material [4]. For the same purpose PIs obtained from 5-(5-(4-(diphenylamino)phenyl)-1,3,4-oxadiazol-2-yl)benzene-1,3-diamine and various aromatic tetracarboxylic dianhydrides: 6FDA, 4,4′-sulfonyldiphthalic anhydride (SDPA), BTDA, 4,4′-oxidiphthalic anhydride (ODPA,), and pyromellitic dianhydride (PMDA) were investigated by Wang et al. [21]. The polyimide from 6FDA showed only oxidation peak. LUMO energy level (−2.13 eV) was calculated from the onset oxidation potential and than HOMO (−5.18 eV) was estimated using LUMO and optical energy band gap values. Expect of polyimides, copolyimides with oxadiazole moieties have been reported in literature as well [22–30]. Posch [22] investigated luminescence (photo- and electroluminescence) properties of copolyimides prepared from 6FDA, BAO and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) with substituents in the bay positions of the perylene core. Most of the polymers were deep red fluorescent in the solid state with λ_{em} at 610 nm. Xu et al. [23] described copolyimides (OPFFx) containing perylene, fluorene and oxadiazole units. These copolymers were prepared from 4,4′-(9H-fluoren-9-ylidene)bisphenylamine (FBPA), BAO, 6FDA and PTCDA with molar ratio of PTCDA/6FDA 5/95 and various molar ratios of BAO/FBPA. The emission spectra of OPFFx in chloroform solution excited by a 493 nm light showed three peaks at 535, 577, and 628 nm, which corresponded to the emission of perylenediimide moieties. Thin film of OPFFx irradiated by ultraviolet light, emitted strong reddish-orange fluorescence. The results from cyclic voltammetry measurements illustrated that OPFFx could be easily reduced (n-doping), which implies that the polymer has the capability for electron injection. Two diamines with 1,3,4-oxadiazole moiety, that is, BAOXD and m-BAOXD have been applied for synthesis of copolymides due to its polyreaction with two dianhydrides, i.e. 4,4′-tetraphthaloyl-bis(1,8-naphthalene dicarboxylic)dianhydride and 6FDA and 4,4′-tetraphthaloyl-bis(1,8-naphthalene dicarboxylic)dianhydride and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDTA) [24,25]. Additionally, polyimides from these monomers have been obtained. Polymers synthesized from bis(ketonaphthalic anhydride) and 6FDA exhibited λ_{em} at 378–392 nm in NMP solution [26,27]. Copolymers obtained from BAOXD and m-BAOXD and NDTA and 6FDA emitted light with λ_{em} at 384 nm in NMP solution and 361 nm in film [28,29]. Rusu et al. [28] described three copolyimides synthesized by polycondensation of BAOXD and m-BAOXD with NDTA and 1,3-bis(4′-phthalic anhydride)tetramethyldisiloxane which emitted light in NMP solution with λ_{em} from 371 nm to 439 nm. The same diamines (BAO, BAOXD and m-BAOXD) have been applied for synthesis of three copolymides from two dianhydrides, that is, 6FDA and PTCDA [29]. The PL spectra of these polymers showed a very strong emission of perylenediimide units, while the emission of oxadiazole moieties was quenched. Damaceanu et al. [30] focused study on copolyimides prepared from NDTA and containing tetramethyldisiloxane units. They emitted light with λ_{em} around 420 nm and exhibited HOMO and LUMO energy levels in the range of −4.55; −5.00 eV and −3.42: −3.56 eV, respectively. In our previous work [18] we reported poly(etherimide) and poly(amideimide) prepared from BAO. They emitted with λ_{em} around 430 nm in NMP solution.

Summarizing, the presented literature review concerns polymers with imide rings and 1,3,4-oxadiazole moieties, it can be concluded that their optical and electrochemical properties make them potential candidates for use as advanced materials in (opto)electronics. Thus, continuing our effort in the synthesis of polyimides with potential applications in organic optoelectronics [8,18,31–36] in this work we present synthesis and studies on new polyimides and copolyimides containing both 1,3,4-oxadiazole and naphthalene imide units derived from NTDA and 4,4′-tetraphthaloylbis(1,8-naphthalene dicarboxylic)dianhydride in the main chain. The presence of a heteroatom with a free electron pair, in this case, the nitrogen atom in oxadiazole unit, gives an opportunity for modification of optical properties of polymers by supramolecular concept based on protonation. The thermal (T_g and thermal stability), optical together with the effect of protonation and electronic properties, that is, orbital energies and resulting energy gap calculated based on cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are presented. Additionally, energy gap was calculated theoretically by density functional theory (DFT). The electronic properties of the material are mainly governed by its electronic band gap (E_g), that is, HOMO–LUMO gap. The magnitude of the E_g and its placement relative to the Fermi level of the metal leads play a significant role in device conductivity [37]. Moreover, herein the spectroelectrochemical behavior of oxadiazole-containing PIs is reported first time. Additionally, the properties of polymers presented in this paper are compared with their analogs bearing acridine moieties which have been described in our previous work [8].