Dyes and Pigments 114 (2015) 110–123

Contents lists available at ScienceDirect

Dyes and Pigments

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

Blue light-emitting polyamide and poly(amide-imide)s containing 1,3,4-oxadiazole ring in the side chain

Corneliu Hamciuc*, Elena Hamciuc, Mihaela Homocianu, Alina Nicolescu, Ionela-Daniela Carja

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, Iasi 700487, Romania

A R T I C L E I N F O

Article history:
Received 26 August 2014
Received in revised form
24 October 2014
Accepted 25 October 2014
Available online 13 November 2014

Keywords:
Polyamides
1,3,4-oxadiazole
High thermostability
Blue fluorescence
High quantum yield
Fluorescence quenching

A B S T R A C T

A new diamine monomer containing a 1,3,4-oxadiazole ring, 4,4′-diamino-4″-[2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole]triphenylmethane, was synthesized and characterized. The diamine is used to prepare novel polyamide and poly(amide-imide)s via a polycondensation reaction with various diacid chlorides in *N*-methyl-2-pyrrolidone. The structures of the monomers and polymers are characterized by means of FTIR, ^{1}H, ^{13}C and ^{15}N NMR spectroscopy. The polymers result in high yields, and exhibit film forming ability and good solubility in many organic solvents. They show high thermal stability, with decomposition temperature being above 420 °C. The optical properties, absorption and fluorescence characteristics, in solution and solid state, are investigated. Solutions of the polymers exhibit fluorescence in the blue region, having high quantum yield in the range of 38.5–58.1%, and large Stokes shift values (110–120 nm). The introduction of hydrochloric acid into the polymer solutions has a significant effect upon the optical properties. Fluorescence quenching in the presence of 2,5-dinitrophenol was analysed using Stern–Volmer equation.

1. Introduction

Aromatic polyamides are among the oldest members of the class of thermally stable polymers. They have received considerable attention with regard to the production of high performance materials, due to their outstanding thermal stability, chemical resistance, and electrical and mechanical properties [1,2]. However, their high glass transition temperature and limited solubility in organic solvents make their processability quite difficult. To overcome these drawbacks to some degree an attractive synthetic approach is the incorporation of bulky substituents such as pendant groups along the polymer backbone [3]. In many cases, the introduction into the macromolecular chains of polyamides of various heterocycles including imide and 1,3,4-oxadiazole rings together with flexible groups led to polymers exhibiting a combination of remarkable properties and processability, particularly in thin films and coatings [4,5].

Heterocyclic polymers containing 1,3,4-oxadiazole rings in the main chain or in the side chain are well known for their high thermal resistance in oxidative atmosphere, good hydrolytic stability, low dielectric constant and tough mechanical properties that make them good candidates for various applications such as high temperature fibres, reinforced materials and membranes for gas separation [6–10]. Particularly interesting are the properties determined by the electronic structure of the 1,3,4-oxadiazole ring because it is characterized by high electron affinity. Due to their electron-withdrawing character which facilitates the injection and transport of electrons, such polymers can be used as promising electron-transporting materials in light-emitting and electronic memory devices [11–15]. The external quantum efficiency in electroluminescence devices with *p*-conjugated polymers, polymers with isolated chromophores and dye-dispersed polymer films can be improved by the introduction of oxadiazole derivative layers between an emissive layer and the cathode of organic light-emitting diodes [16].

Much research is made in developing blue light-emitting polymer materials with high thermal stability and high emission efficiency. A blue light-emitting device can generate all colours by using the appropriate dyes, in comparison with green or red which cannot emit blue light in this way [17]. One approach to develop such structures is the introduction in the main chain or in the side chain of the chromophore segments which emit blue light. Polymers with a well defined conjugation length can be obtained,

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* Corresponding author.
E-mail address: chamciuc@icmpp.ro (C. Hamciuc).

http://dx.doi.org/10.1016/j.dyepig.2014.10.018

which is highly desired, taking into account that a larger distribution of conjugation length leads to a larger broadness of the emission bands [17–21].

Among the efficient organic luminophors 2,5-diphenyl-substituted-1,3,4-oxadiazoles are known to emit light in the blue region. This can be explained by the effect of the 1,3,4-oxadiazole ring which is close to that of *p*-phenylene group in a conjugated aromatic system [22]. 2,5-diaryl-1,3,4-oxadiazoles are similar to polyphenyl hydrocarbons with the corresponding number of aromatic nuclei. Electron donor substituents like *p*-dimethylamino group can significantly raise the fluorescence intensity in comparison with electron acceptor substituents. Also, the incorporation of electron donor substituents in the structure of 2,5-diaryl-substituted oxadiazoles gives large absorption shifts and photoluminescence spectra toward longer wavelength, as well as a greater Stokes shift [23].

From previous investigations it was concluded that certain polymers containing dimethylamino substituents in the *para*-position of the pendant chromophoric 2,5-diphenyl-1,3,4-oxadiazole unit are promising candidates for emissive materials in light-emitting devices [24]. The substituted diphenyl-1,3,4-oxadiazole units are able to transport holes as well as electrons and show an intense fluorescence. Thus, in our laboratory were developed poly(1,3,4-oxadiazole-ether-imide)s [25,26], poly(1,3,4-oxadiazole-imide)s [27] and poly(1,3,4-oxadiazole-ester-imides) [28] which were synthesized by a polycondensation reaction of 2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole with certain aromatic dianhydrides, such as 1,1,1,3,3,3-hexafluoro-2,2-bis-[(3,4-dicarboxy phenoxy)phenyl]propane dianhydride, 2,2′-bis-[(3,4-dicarboxy-phenoxy)phenyl]-1,4-phenylenediisopropylidene dianhydride, bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride, and 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate) dianhydride. The obtained polymers exhibited fluorescence in the blue region when excited with UV light. The presence of the heteroatom with a free electron pair, in this case the nitrogen atoms in the oxadiazole rings and dimethylamino groups, gives the opportunity for protonation with hydrochloric acid (HCl) that may change the optical properties [29].

In this paper we describe the synthesis and characterization of a new diamine containing 1,3,4-oxadiazole ring, 4,4′-diamino-4″-[2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,5-oxadiazole]-triphenylmethane. Novel polyamide and poly(amide-imide)s were prepared by polycondensation reaction of the new diamine with various diacid chlorides. The properties of the resulting polymers, such as solubility, thermal and optical characteristics were investigated. The polymers exhibited high thermal stability and pure blue light emission.

2. Experimental

2.1. Materials

4-Dimethylaminobenzhydrazide, **1**, 4-fluorobenzoyl chloride, **2**, 4-hydroxybenzaldehyde, terephthalic acid, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, 4-aminobenzoic acid, 4-bromo-*o*-xylene, dimethyldichlorosilane, aniline, aniline hydrochloride, phosphorus oxychloride ($POCl_3$), potassium carbonate (K_2CO_3), thionyl chloride, *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and pyridine were provided from Aldrich and used as received.

2.2. Characterization

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). The inherent viscosity (η_{inh}) of the polymers was determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20 °C, at a concentration of 0.5 g dL^{-1}. The molecular weight was determined by gel permeation chromatography (GPC) using UV and SLS detectors and PLgel 5micro Mixed C Agilent and PLgel 5micro Mixed D Agilent Columns. Measurements were carried out with polymer solutions in DMF by using DMF as eluent. Polystyrene standards of known molecular weight were used for calibration. FTIR spectra were recorded on a Bruker Vertex 70 at frequencies ranging from 400 to 4000 cm^{-1} using KBr pellets or films. The NMR spectra were recorded on a Bruker Avance III 400 spectrometer operating at 400.1, 100.6 and 40.6 MHz for ^1H, ^{13}C, and ^{15}N nuclei, respectively. Samples were recorded with either a 5 mm multinuclear inverse detection z-gradient probe (^1H spectra and all H–C/H–N 2D experiments) or with a 5 mm four nuclei direct detection z-gradient probe (^{13}C spectra). All the experiments were recorded using standard pulse sequences, in the version with z-gradients for 2D spectra, as delivered by Bruker with TopSpin 2.1 PL6 spectrometer control and processing software. Chemical shifts are reported in δ units (ppm) and were referenced to the internal deuterated solvent for ^1H and ^{13}C chemical shifts (DMSO referenced at ^1H: 2.51 ppm and ^{13}C: 39.47 ppm) and referenced to liquid ammonia (0.0 ppm) using nitromethane (380.2 ppm) as external standard for ^{15}N chemical shifts. Atomic Force Microscopy (AFM) images were taken in air, on an SPM SOLVER Pro-M instrument. A NSG10/Au Silicon tip with a 35 nm radius of curvature and 255 kHz oscillation mean frequency was used. The apparatus was operated in semi-contact mode, over a 2 × 2 μm^2 scan area, 256 × 256 scan point size images being thus obtained. Thermogravimetric analysis (TGA) was carried out in nitrogen, at a heating rate of 10 °C min^{-1}, using a Mettler Toledo TGA/SDTA 851^e balance. The heating scans were performed on 2–5 mg of sample in the temperature range of 25–900 °C. Alumina crucible (70 μL) is used as sample holder. The initial decomposition temperature is characterized as the temperature at which the sample achieves 5% weight loss. The temperature of 10% weight loss (T_{10}) and the temperature of maximum decomposition rate which is the maximum signal in differential thermogravimetry (DTG) curves were also recorded. Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 1 (Mettler Toledo, Switzerland) operating with version 9.1 of Stare software. The samples were encapsulated in aluminium pans having pierced lids to allow escape of volatiles. The heating rate of 10 °C min^{-1} and nitrogen purge at 120 mL min^{-1} was employed. Heat flow *versus* temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. UV–Vis absorption and photoluminescence (PL) spectra were recorded with an Analytik Jena – Specord 200 spectrophotometer and a Perkin–Elmer LS55 luminescence spectrofluorimeter, respectively. All solvents used in the present paper were spectrophotometric grade. Quenching studies were carried out by adding small amounts of the quencher (3,5-dinitrophenol) to the studied polymer in DMAc solution. PL spectra were recorded after each addition. All measurements were performed at room temperature. For PL measurements polymer films were prepared by using 1% polymer solutions in NMP, which were spin-coated on quartz slides at about 1000 rpm, for 30 s, at room temperature.

2.3. Synthesis

2.3.1. N-(4-dimethylaminobenzoyl)-N′-(4-fluorobenzoyl)hydrazine (**3**)

4-Dimethylaminobenzhydrazide (8.95 g, 0.05 mol), NMP (65 mL) and pyridine (4.0 mL) were placed in a 100 mL three-necked flask equipped with mechanical stirrer, and the mixture was stirred until complete dissolution was achieved. The solution was cooled to 0 °C, and 4-fluorobenzoyl chloride (7.925 g, 0.05 mol)