

# Synthesis and photophysical study of some new highly thermostable blue fluorescent poly(1,3,4-oxadiazole-imide)s containing dimethylamine groups



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## ABSTRACT

New poly(1,3,4-oxadiazole-imide)s were synthesized from a diamine containing 1,3,4-oxadiazole ring, 4,4'-diamino-4''-[(2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole]triphenylmethane, and different aromatic dianhydrides: 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 9,9-bis[(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride, 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) and perylene-3,4,9,10-tetracarboxylic dianhydride. The polymers were easily soluble in polar organic solvents and exhibited high thermal stability, having 5% weight loss in the range of 445–470 °C and glass transition temperature in the domain of 201–244 °C. The optical properties were investigated in different media. The absorption characteristics (intensity, absorption maximum and shape) of investigated compounds depended on their chemical structures and the nature of environment. The emission of these samples was represented by one broadened and blue emission band. The largest and solvent dependent Stokes shifts values were obtained. The fluorescence quantum yield (QY) values of polymer with hexafluoroisopropylidene groups, in tetrahydrofuran solution, depended on the wavelength used for excitation. This is an exception from Kasha's rule and Vavilov's law, which was attributed either to photodecomposition or to the enhancement of intramolecular energy transfer process competing with internal conversion between singlet states. High QY values were obtained for polymers with isopropylidene or fluorene units in dimethyl sulfoxide (polar solvent), which may be due to the strong overlap of electronic transitions of species from system.

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## 1. Introduction

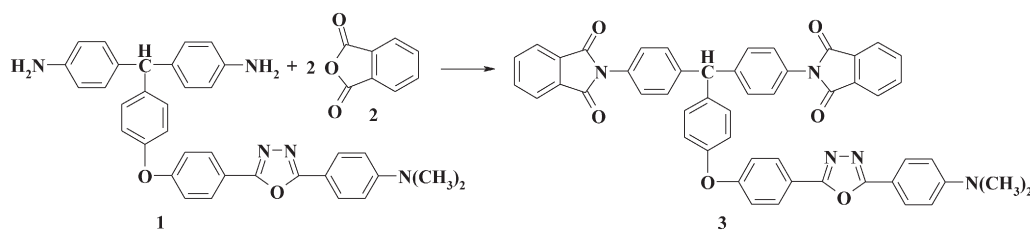
Aromatic polyimides are a class of polymers known for their high thermal stability, high glass transition, low thermal expansion coefficient, high radiation resistance, low dielectric constant, excellent mechanical properties, and good chemical resistance. The excellent physical properties result from rigid polymer structures and strong intermolecular interactions [1,2]. These polymers have been widely used in aerospace and automotive industries, and as interlayer dielectric insulators in microelectronics. They were studied for applications in advanced technologies as gas separation membranes, polymer matrix for composites and nanocomposites, fuel cells, photovoltaics, and materials having electroluminescent characteristics [3,4]. However, the applications of most polyimides are limited due to their insolubility in conventional solvents and extremely high glass transition temperature which make their processing very difficult. Various efforts have been made on the synthesis of soluble and processable polyimides without much sacrifice of their excellent thermostability. The aromatic ether linkages inserted into the

aromatic main chains of the polyimides lead to lower glass transition temperature as well as significant improvement of solubility [5–7]. Also, the incorporation of hexafluoroisopropylidene (6F) groups into polymer backbones enhances the polymer solubility without sacrificing thermal stability [8–10]. Therefore, polyetherimides and fluorinated polyimides were studied as high performance materials having both high performance characteristics and good processability.

The presence of 1,3,4-oxadiazole rings in the macromolecular chains of polymers improves their properties such as thermo-oxidative and chemical stability, strength, stiffness, that makes them good candidates for various applications. Particularly interesting are properties determined by their electronic structure because they are characterized by high electron affinity. Their electron-withdrawing character facilitates the injection and transport of electrons being thus used as material for light-emitting diodes [11–12]. Poly(1,3,4-oxadiazole imide)s can be prepared by using two methods. The first method implies two steps: the reaction of an aromatic dianhydride with a diamine containing preformed 1,3,4-oxadiazole ring resulting a poly(amic acid) that can be cyclodehydrated in the second step to the corresponding imide structure [13]. The other method consists in the cyclodehydration at elevated temperature of poly(hydrazide imide)s [14].

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Scheme 1. Preparation of model compound 3.

Nowadays, novel fluorescent materials have been developed for applications in light-emitting diodes. Much research has been directed towards studying blue light-emitting polymer materials with high thermal stability and high emission efficiency. The glass transition temperature of polymers is also an important property for these applications [15]. One approach to develop such structures is the introduction of blue light-emitting chromophore segments in the main or side chains of polymers. Heterocyclic thermostable polymers are studied as potential luminescent polymers due to their high glass transition temperature and thermal and chemical stability, essential characteristics required in many applications as emissive materials [16]. In our laboratory different classes of blue fluorescent polymers containing 1,3,4-oxadiazole groups were developed. Thus, highly fluorinated thermostable poly(1,3,4-oxadiazole-ether)s containing bis(*p*-phenyl)-1,3,4-oxadiazole segments and 3-trifluoromethylphenyl-2,2,2-trifluoroethane or 3,5-difluoromethylphenyl-2,2,2-trifluoroethane units were prepared [17]. They exhibited fluorescence in the blue region when excited with UV light of 300–340 nm. Their fluorescence properties were influenced by the solvent nature, excitation wavelength and protonation. The solvatochromic properties in the binary solvent environments were predominantly influenced by the acidity and basicity of the solvent systems [18]. It is known that 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 [19–21]. The substituted diphenyl-1,3,4-oxadiazole units are able to transport holes as well as electrons and show an intense fluorescence [22]. Therefore, we investigated polyamide and poly(amide imide)s having 2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole pendant groups which showed excellent fluorescence both in solution and in solid state. Solutions of the polymers exhibit fluorescence in the blue region, with high quantum yield in the range of 38.5–58.1%, and large Stokes shift values (110–120 nm). Protonation with HCl as a dopant caused a significant decrease of fluorescence intensity. Fluorescence quenching in the presence of 2,5-dinitrophenol was analyzed using Stern-Volmer equation [23].

In our continuous efforts to obtain new polyimides with enhanced solubility and a good combination of properties for future advanced applications as potential luminescent polymers, we considered that it would be interesting to introduce 2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole groups in the side chain in order to improve the optical properties of the polymers maintaining their thermal stability. Thus, this article presents the synthesis and characterization of novel blue fluorescent polyimides based on a diamine containing 1,3,4-oxadiazole ring and various aromatic dianhydrides exhibiting different degrees of flexibility. The aim of this work is to establish new correlations between the structure and physical properties of the polymers. The basic properties such as solubility, molecular weight, thermal stability and glass transition temperature were investigated. A study on the photo-optical properties was performed with the purpose of establishing structure–property relationships. The modification of the optical properties by doping with HCl was also described.

## 2. Experimental

### 2.1. Materials

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (6HDA) and perylene-3,4,9,10-tetracarboxylic dianhydride (PEDA) were provided from Aldrich. All other reagents were used as received from commercial sources or were purified by standard methods. 2,5-Bis(*p*-aminophenyl)-1,3,4-oxadiazole was prepared by the reaction of *p*-aminobenzoic acid with hydrazine hydrate, in polyphosphoric acid [24].

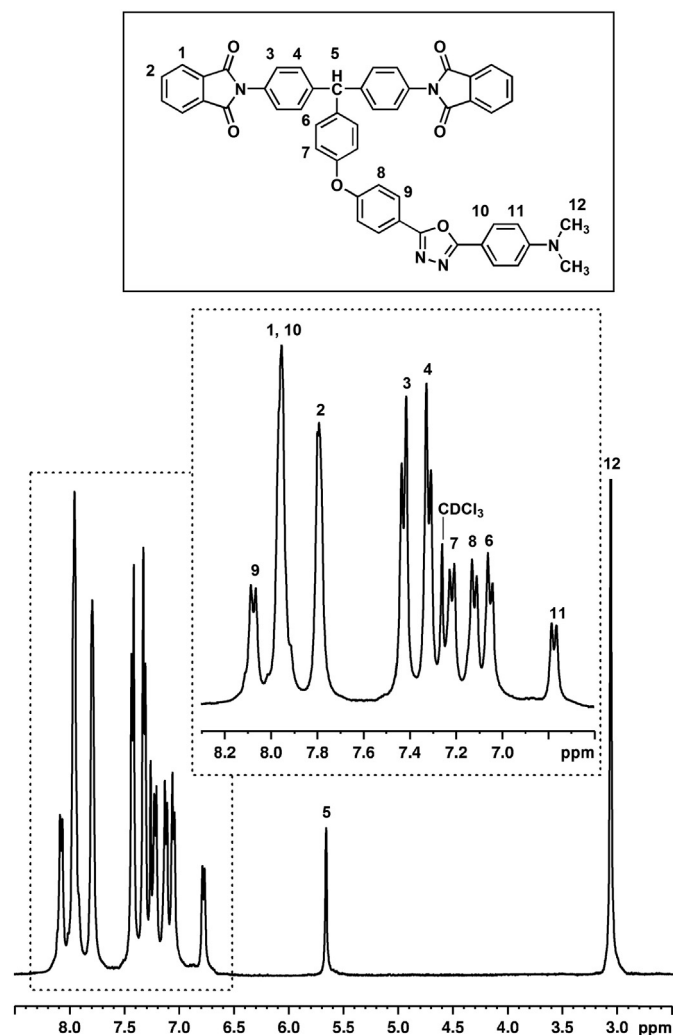


Fig. 1.  $^1\text{H}$  NMR spectrum of model compound 3 (400 MHz,  $\text{CDCl}_3$ ).

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