Journal of Luminescence 130 (2010) 2242–2246

Contents lists available at ScienceDirect

Journal of Luminescence

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

Luminescence property of poly(1,3-bis(phenyl-1,3,4-oxadiazole))s containing polar groups in the main chain

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ARTICLE INFO

Article history:
Received 12 February 2010
Received in revised form
25 June 2010
Accepted 29 June 2010
Available online 17 July 2010

Keywords:
Polyoxadiazole
Electron carrier
Photoluminescence
Electroluminescence
Thermal stability

ABSTRACT

Photoluminescence properties of a new series of soluble 1,3-bis(phenyl-1,3,4-oxadiazole)s bearing polar groups in the main chain like $-NO_2$, $-OH$, $-CH_3$ and –Cl have been studied. The photoluminescence spectra show significant shift in the emission wavelengths in solid as well as in solution depending on the groups attached in the main chain, both redshift (electron withdrawing group) and blueshift (electron donating group) and change in the intensity of the emissive spectra as compared with those of the simple polyoxadiazoles at ~300 nm. Quantum yield measurement with reference to anthracene indicates increase in the quantum efficiency many folds with decrease in concentration. The polymers are found to be thermally stable up to 350–400 °C and their glass transition temperature ranges between 100 and 150 °C.

1. Introduction

In designing organic light emitting diodes (OLEDs), a luminescent material is required in which electron and hole are recombined, resulting in the emission of light. In a multilayer device electrons are injected by cathode and holes by anode when an electric field is applied across the surface of the luminescent material. Many highly fluorescent organic materials are developed to produce three basic colours i.e. red, green and blue for a full colour display in electroluminescence. Electron mobility in organic materials is found to be an order of magnitude lower than hole mobility [1–7].

In particular, attention has been drawn towards poly(1,3,4-oxadiazole)s as electron transporting material, thermally stable with a high quantum yield of luminescence. But poly(1,3,4-oxadiazole)s lack sufficient solubility in common organic solvents and hence processibility due to its rigid structure [8–10].

Poly(1,3,4 oxadiazole)s are made soluble by attaching flexible ether linkage and perfluoryl or diphenyl silyl linkage of nonpolar cardo type moiety. Poly(1,3,4 oxadiazole)s emit blue–green and blue light in electrolumionescence [11–18]. Oxadiazole moiety is a good electron transporter, thereby increasing the quantum yield of fluorescence. Polyoxadiazole containing carbazole, polyfluorene, and phosphonated moiety are soluble in organic solvent and shows high quantum yield of fluorescence [19–24].

In this paper we have studied soluble oligomeric poly(1,3-bis(phenyl-1,3,4-oxadiazole))s containing non-symmetric moiety (isophthalic moiety) and polar functional groups ($-NO_2$, $-Cl$, $-OH$, $-CH_3$) in the main chain. The effect of polar groups on photoluminescence and thermal property is discussed.

2. Experimental

Poly(1,3-bis(phenyl-1,3,4-oxadiazole))s containing non-symmetric moiety (isophthalic moiety) and polar end groups ($-NO_2$, $-Cl$, $-OH$, $-CH_3$) in the main chain were synthesized and characterized in the same way as reported earlier elsewhere [25]. Synthesis of 1,3-bis(phenyl-1,3,4-oxadiazole)s containing non symmetric moiety (isophthalic moiety) and polar end groups ($-NO_2$, $-Cl$, $-OH$, $-CH_3$) in the main chain is accomplished through the cyclization of polyhydrazides through chemical means. Polyhydrazides are synthesized from isophthalic acid chloride and isophthalic acid hydrazide through polycondensation at low temperature followed by the reaction with the esters of the compounds carrying the polar end groups. The reaction was carried out at 80 °C for 24 h. Isophthalic acid chloride based polyhydrazides in NMP was added to the solutions of methyl 4-nitrobenzoate, methyl 4-hydroxybenzoate, methyl 4- chlorobenzoate and p-toluyl chloride with pyridine as a catalyst. The product was precipitated in water. White powdery polhydrazides with polar end groups were cyclized chemically in the presence of phosphorous oxychloride and again precipitated in ice cold water.

UV–visible absorption spectra were taken on a Shimadzu UV-2500 spectrophotometer. Photoluminescence spectra were recorded using a Hitachi F-2500 spectrophotometer. Luminescence quantum yield of the polymers is determined from the

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0022-2313/$ - see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jlumin.2010.06.027

PL spectral data taking a standard fluorescence sample anthracene as the reference as it emits in the region similar to that that of the polymers we have synthesized. The maximum intensity of emission at different concentrations is considered for the quantum yield calculations. The fluorescence quantum yield of anthracene is taken as 0.27 as per literature and it emits in the region 360–480 nm [26]. The quantum yield of a polymer sample in solution φ_s relative to a reference sample of known quantum yield φ_r may be related as [27]

$$\varphi_s = \varphi_r \left(\frac{A_r}{A_s}\frac{I_s}{I_r}\right) \quad (1)$$

where A_s and A_r are the absorbance of the sample and reference solutions, respectively, at the excitation wavelength; I_r and I_s are the corresponding relative integrated fluorescence intensities.

Thermal analyses were performed using a Shimadzu TA-30 and a Shimadzu DSC-60 instrument at the heating rate of 10 °C/min in N_2 atmosphere.

3. Results and discussion

3.1. Polymer properties

The structure of the polymer is shown in Fig. 1 and the physical properties are summarized in Table 1. The polymers are soluble in organic polar solvents like DMAc, DMF, NMP and DMSO and partly soluble in THF. Their inherent viscosity is in the range 0.16–0.43 dL/g using DMAc as solvent at 0.5% concentration of the polymer at room temperature. The GPC result of the weight average molecular weight of the soluble part of the polymers in THF ranges between 17,588 and 26,521 Da. The polymers are found to be thermally stable up to 350–400 °C, and their glass transition temperature ranges between 100 and 150 °C.

3.2. Optical band gap and UV absorption

Optical band gaps of the polymers are calculated from the λ onset value using the relation band gap $E_g = hc/\lambda$ [28].

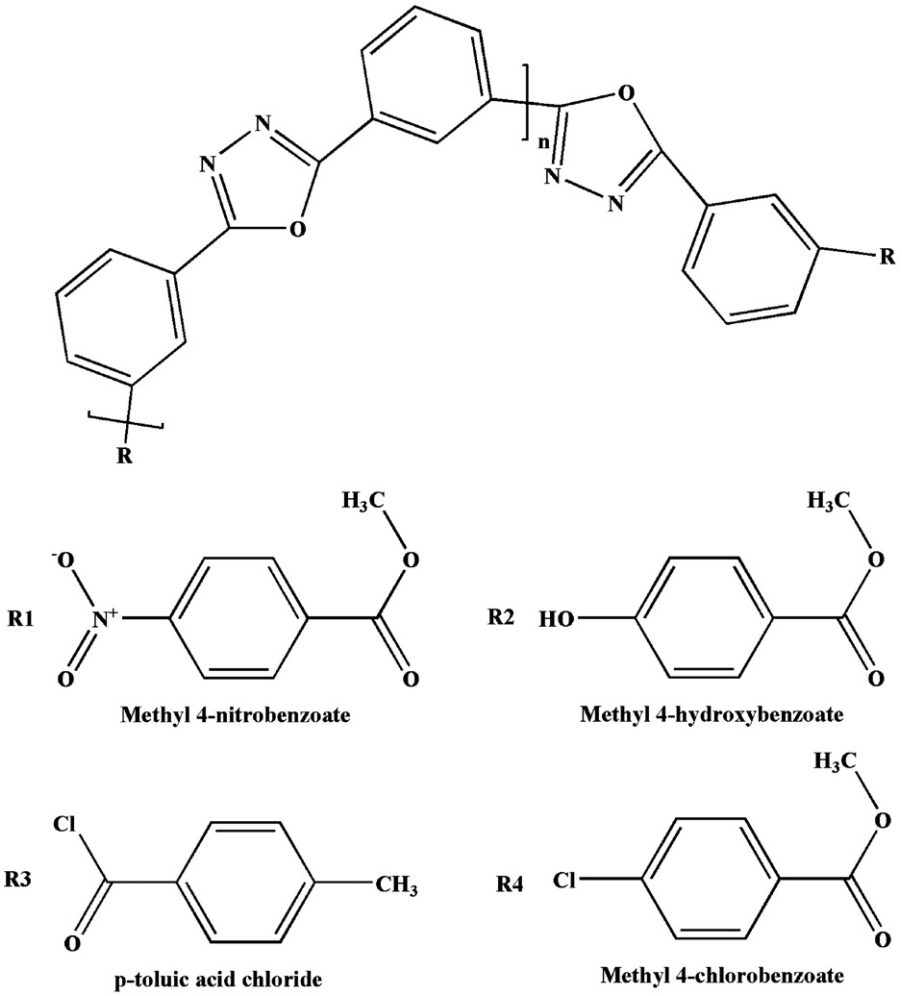

Fig. 1. Structure of 1,3-bis(phenyl-1,3,4-oxadiazole)s.

Table 1
Physical properties of polymers.

Inherent viscosity (dL/g)	Melting point (°C)	Degradation temperature (°C)	Glass transition temperature T_g (°C)	Oxidation potential (V)	Reduction potential (V)	Band gap (eV)
0.16–0.43	< 320	380	122	3.0	−2.0	2.45