

Contents lists available at ScienceDirect

Reactive and Functional Polymers



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

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



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

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

ARTICLE INFO

Article history: Received 5 December 2015 Received in revised form 24 March 2016 Accepted 30 March 2016 Available online 2 April 2016

Keywords: Polyimide 1,3,4-Oxadiazole ring Dimethylamine groups, Thermal stability Blue fluorescence

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[(3,4dicarboxyphenoxy)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

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



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(1,3,4oxadiazole-ether)s containing bis(p-phenyl)-1,3,4-oxadiazole segments and 3-trifluoromethylphenyl-2,2,2-trifluoroethane or 3,5ditrifluoromethylphenyl-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-1,3,4oxadiazole unit are promising candidates for emissive materials in lightemitting 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)-1,3,4oxadiazole 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-(4dimethylaminophenyl)-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. ¹H NMR spectrum of model compound 3 (400 MHz, CDCl₃).





9,9-Bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride (FLDA) was synthesized according to the literature using a threestep synthetic procedure starting from the nitro-displacement reaction



Fig. 3. FTIR spectra of polymers 4.

of 4-nitrophthalonitrile with 9,9-bis(4-hydroxyphenyl)fluorene, in dry *N*,*N*-dimethylformamide (DMF), in the presence of potassium carbonate, at room temperature, followed by alkaline hydrolysis of the tetranitrile intermediate and dehydration with acetic anhydride of the resulting tetracarboxylic acid [25,26]. M.p.: 252–254 °C. FTIR (KBr, cm⁻¹): 1840, 1775, 1600, 1248. ¹H NMR (400 MHz, DMSO- d_{6} , δ): 7.11 (4H, m), 7.28 (4H, m), 7.45 (4H, m), 7.52 (4H, m), 7.75 (2H, d), 7.97 (2H, m), 8.02 (2H, d).

4,4'-Diamino-4"-[2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole)]triphenylmethane (1) was prepared by nucleophilic substitution reaction of a fluorinated compound, namely 2-(4-dimethylaminophenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole, with 4,4'-diamino-4"-hydroxytriphenylmethane, as it was previously reported [23]. The fluorinated compound was obtained by reacting 4dimethylamino-benzhydrazide with *p*-fluorobenzoyl chloride, and cyclodehydration of the resulting product with POCl₃. M.p.: 205-207 °C. FTIR (KBr, cm⁻¹): 3436, 3350, 3030, 2890, 1611, 1508, 1241, 1013, 956. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 3.00 (6H, s), 4.93 (4H, bs), 5.72 (1H, s), 6.52 (4H, d), 6.78 (4H, d), 6.83 (2H, d), 7.03 (2H, d), 7.14 (4H, d), 7.87 (2H, d), 8.05 (2H, d).

2.2. Synthesis of the model compound (3)

Diamine 1 (0.553 g, 1 mmol), phthalic anhydride (2) (0.296 g, 2 mmol) and glacial acetic acid (6 mL) were introduced into a flask



Fig. 4. ¹H NMR spectrum of polymer 4e.

and heated at reflux temperature (120 °C) for 8 h. The reaction mixture was cooled to room temperature and the solid was filtered, washed with water and methanol and dried at 80 °C for 10 h. Yield: 90%. FTIR (KBr, cm⁻¹): 3060, 1770, 1723, 1601, 1370, 1241, 1014, 981, 720. ¹H NMR (400 MHz, DMSO- d_6 , δ): 8.12 (2H, s), 7.92 (8H, s), 7.78 (4H, d), 7.45 (4H, d), 7.35 (4H, d), 7.24 (2H, d), 7.12 (2H, d), 7.05 (2H, d), 6.85 (2H, d), 5.70 (1H, s), 3.1 (6H, s).

2.3. Preparation of the polymers (4)

The polymers 4a, 4b and 4c were prepared by a two-step polycondensation reaction of aromatic diamine containing 1,3,4-oxadiazole ring, 1, with different aromatic dianhydrides, such as 6FDA, 6HDA, and FLDA, respectively. Polyimide 4d was synthesized starting from diamine 1 and a mixture of dianhydrides 6FDA/PEDA (0.85/0.15 M ratio), while polyimide 4e was obtained by reacting 6FDA with an equimolecular amount of 1 and 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole. A typical polycondensation reaction was run as shown in the following example for 4c: In a 100 mL three-necked flask equipped with mechanical stirrer and nitrogen-inlet and outlet were introduced diamine 1 (0.387 g, 0.7 mmol) and *N*-methyl-2-pyrrolidinone (NMP) (6 mL). The mixture was stirred under nitrogen to the complete dissolution. The dianhydride FLDA (0.45 g, 0.7 mmol) was added to the resulting solution and stirring was continued for 10 h. Then 3 mL pyridine and 3 mL acetic anhydride were added into the flask, and the solution was heated at 100 °C for 4 h. The flask was cooled-down to room temperature and the solution was poured into water to precipitate the polymer. The solid product was filtered, washed three times with water under stirring and dried at 100 °C.

Polymer 4d was prepared using another procedure. 1 (0.553 g, 1 mmol), 6FDA (0.377 g, 0.85 mmol), PEDA (0.058 g, 0.15 mmol), NMP (14 mL) and LiCl (0.525 g) were introduced into a flask and the mixture was heated under stirring and inert atmosphere at 180–200 °C, for 6 h. The flask was cooled-down to room temperature and the polymer was isolated by precipitation with water. It was filtered, washed three times with water under stirring, and then it was dried at 100 °C.

2.4. Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices).

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GPC results and thermal characteristics of polymers 4.	
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Sample	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_w/M_n	T_g (°C)	<i>T</i> ₅ (°C)	<i>T</i> ₁₀ (°C)	<i>T</i> _{max1} (°C)	$T_{\max 2}$ (°C)	Char yield at 700 °C (%)
4a	16,200	20,800	1.28	-	460	508	554	623	61.2
4b	22,800	32,100	1.41	201	470	520	536	590	48.7
4c	18,500	25,700	1.39	244	465	494	504	577	61.7
4d	-	-	-	-	445	480	553	-	50.4
4e	18,500	25,300	1.37	220	460	489	543	620	56.8



Fig. 5. TG curves of polymers 4.

The infrared spectra were recorded on a FTIR Bruker Vertex 70 Spectrophotometer at frequencies ranging from 4000 to 400 cm⁻¹. Samples were mixed with KBr and pressed into pellets.

¹H NMR (400 MHz) spectra were obtained at room temperature on a Bruker Advance DRX spectrometer, using CDCl₃ as solvent.

The molecular weights and their distribution were determined by gel permeation chromatography (GPC) with a PL-EMD 950 evaporative mass detector instrument. Two poly(styrene-*co*-divinylbenzene) gel columns (PLgel 5 μ m Mixed-D and PLgel 5 μ m Mixed-C) were used as stationary phase while DMF was the mobile phase. The eluent flow rate was 1.0 mL min⁻¹. Polystyrene standards of known molecular weight were used for calibration.

Table 2

Positions of absorption wavelengths, λ_{max}^{abs} (nm), excitation wavelengths, λ_{max}^{ex} (nm), emission wavelengths, λ_{max}^{em} (nm) maxima, Stokes shifts (SS, nm), emission quantum yields (QY%) values for investigated samples in different solvents ($c = 1.57 \times 10^{-5}$ mol L^{-1} (for absorption measurements) and $c = 2.59 \times 10^{-5}$ mol L^{-1} (for emission measurements)).

Sample	Medium	$\lambda_{max}{}^{abs}$, nm	λ_{\max}^{ex} ,	λ_{\max}^{em} , nm	SS,	QY, %
			nm		nm	
3	THF	333	-	417	84	25.36
	DCM	334	268, 334	414	80	-
	NMP	341	274, 345	452	111	-
	DMSO	340	276, 344	463	123	28.29
4a	THF	255ª, 336	273, 335	420	84	8.73
	DCM	255ª, 338	276, 340	419	81	-
	NMP	341	276, 345	453	112	-
	DMSO	344	276, 345	463	115	8.24
4b	THF	247, 331	272, 335	419	88	17.72
	DCM	247, 336	275, 335	417	81	-
	NMP	339	279, 346	454	115	-
	DMSO	338	277, 346	465	127	22.92
4c	THF	234, 309, 333	273, 335	419	86	17.61
	DCM	244, 309, 336	274, 335	414	78	-
	NMP	309, 339	276, 346	454	115	-
	DMSO	310, 338	276, 346	469	126	23.46
4d	THF	257, 334	-	417, 527 ^b ,566 ^b	83	13.34
	DCM	266 ^a , 334,483 ^b , 518 ^b	273, 334	413, 532 ^b , 570 ^b	79	-
	NMP	341, 484 ^b , 523 ^b	276, 346	451, 534 ^a	110	-
	DMSO	341, 490 ^b , 525 ^b	274, 346	462	121	8.85
4e	THF	315	273, 335	417	102	5.39
	DCM	334	273, 342	413	79	-
	NMP	312	275, 346	450	138	-
	DMSO	340	277, 345	456	116	5.78

^a Shoulder.

^b Bands with a weak intensity.

Differential Scanning Calorimetry (DSC) was performed on a Mettler Toledo DSC822e. Approximately 10 mg of sample were tested applying a heating rate of 10 °C min⁻¹ from 20 to 200 °C, in air (50 mL min⁻¹). Heat flow vs. temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The midpoint of the inflexion curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers.

Thermal stability was analyzed by means of a Mettler Toledo TGA-SDTA851e derivatograph. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded in nitrogen, with a flow of 20 mL min⁻¹ in the temperature interval 25–700 °C and with heating rate of 10 °C min⁻¹. Constant operational parameters were preserved for all the samples, which had the mass ranged between 1.8 and 4 mg, so as to obtain comparable data.

The UV—VIS electronic absorption spectra of 3 and of the polymers were measured with a Shimadzu UV 3600 absorption spectrometer, in tetrahydrofuran (THF), dichloromethane (DCM), NMP, and dimethyl sulfoxide (DMSO) solutions. The fluorescence excitation and emission spectra were obtained using a LS 55 PerkinElmer spectrometer. All used solvents were spectroscopic grade.

The fluorescence quantum yields, QY, were determined using FLS 980 apparatus equipped with a Quanta-phi integrating sphere accessory, using solutions with absorbance lower than 0.1. Both the sample and reference were excited at the same wavelength. All the measurements were performed at room temperature.

3. Results and discussion

3.1. General characterization of model compound (3) and poly(1,3,4-oxadiazole-imide)s (4)

The model compound 3 was prepared starting from 1 and phthalic anhydride (2), in glacial acetic acid, as shown in Scheme 1. The structure of 3 was identified by FTIR and ¹H NMR spectroscopy. Fig. 1 presents the ¹H NMR spectrum of 3 with the assignment for all the protons. The protons in *ortho* position to 1,3,4-oxadiazole or imide rings appeared at the highest ppm values due to the electron withdrawing characteristic of these heterocycles. Aliphatic protons of N(CH₃)₂ groups appeared at around 3.1 ppm, while aliphatic proton of CH group appeared at 5.70 ppm.

The polymers 4a, 4b and 4c were synthesized by a two-step polycondensation reaction. In the first step the intermediates poly(amic acid)s were synthesized by the polycondensation reaction of equimolar amounts of 1 and dianhydrides 6FDA, 6HDA or FLDA, at room temperature, in NMP as solvent. The concentration of the reaction mixture was adjusted to around 10-12% w/w. In the second step acetic anhydride and pyridine were added to these solutions and the resulting mixtures were heated at 100 °C in order to perform chemical cyclization of poly(amic acid)s to fully cyclized polyimides. Polymer 4e was prepared by using the same two-steps polycondensation reaction starting from 6FDA and equimolar amounts of 1 and 2,5-bis(p-aminophenyl)-1,3,4oxadiazole. Due to the low reactivity and insolubility of PEDA in organic solvents, polymer 4d was prepared in one step, at high temperature, using as solvent NMP containing 3.5% LiCl, following a method previously reported [27]. The chemical structures of the polymers were illustrated in Fig. 2.

The structure of polymers was confirmed by FTIR and ¹H NMR spectroscopy. The FTIR spectra of polymers 4 are shown in Fig. 3. The complete disappearance of the absorption bands of 1660–1670 and 2500–3000 cm⁻¹ characteristic for *o*-carboxy-amide groups of poly(amic-acid)s confirms the complete cyclization of these compounds to fully cyclized polyimide structure. In all spectra characteristic absorption bands appeared at around 1240 cm⁻¹ due to aromatic -C-O-C- linkages. The absorption bands appearing at around 1020 and 980 cm⁻¹ were assigned to oxadiazole rings while the

bands appearing at 2920 and 2860 cm⁻¹ are characteristic to aliphatic groups. Absorptions bands of imide rings appeared at 1770–1780 and 1720–1730 cm⁻¹ (C=0 of imide asymmetric and symmetric stretching vibrations), 1360–1370 cm⁻¹ (C=N stretching vibrations in imide ring) and 730–740 cm⁻¹ (C=0 bending of imide ring). Aromatic C=H absorptions were found at 3070 cm⁻¹ while aromatic C=C absorptions were found at 1600 and 1500 cm⁻¹. In the FTIR spectra of 4a, 4d and 4e the absorption bands appearing at 1210 and 1180 cm⁻¹ were assigned to hexafluoroisopropylidene groups. In the case of 4d, a characteristic absorption band was observed at 1665 cm⁻¹ due to symmetric stretching of C=O in the six member of imide ring.

The ¹H NMR spectra of the polymers showed characteristic peaks for aliphatic protons of diamine segments at 5.72 ppm (CH of triphenylmethane groups) and at 3.00 ppm (N(CH₃)₂ groups). Fig. 4 presents the ¹H NMR spectrum of copolymer 4e with the assignment for all the protons, according to the numbering scheme presented in the interior figure. The structure of 4e was determined by calculating the integral values of protons 9 and 14 and the ratio between these two values. It was found that the composition of the polymer is similar with the composition of the reactants used for the synthesis. The structure of 4d was not confirmed by this method due to the low solubility of this polymer in organic solvents.

The model compound 3 and the polymers 4b, 4c and 4e were easily soluble in organic solvents such as NMP, DMF and chloroform. Polymer 4a was soluble in NMP and DMF but it was less soluble in chloroform, probably due to a higher rigidity of the macromolecular chains. Polymer 4d exhibited less solubility in organic solvents. Thus, this polymer was soluble in NMP, partially soluble in DMF and insoluble in chloroform, probably due to the presence in the chemical structure of the units derived from perylene dianhydride.

The molecular weight of the polymers was determined by GPC. The values of weight-average molecular weight (M_w) were in the range of 20,800–32,100 g mol⁻¹, the number-average molecular weight (M_n) were in the range of 16,200–22,800 g mol⁻¹ and the polydispersity M_w/M_n was in the range of 1.28–1.41 (Table 1). The molecular weight

of the polymer 4d was not determined by GPC due to its low solubility in organic solvents.

3.2. Thermal properties

The glass transition temperature (T_g) of the present polymers, evaluated from DSC curves, was in the range of 201–244 °C (Table 1). The DSC measurements showed no evidence of crystallisation or melting which proves an amorphous morphology. Generally, T_g of polymers depends on chain rigidity. The polymer 4a did not show a T_g in the interval of measurements. This is due to the presence of 6F groups and pendant 2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole units which increased the rigidity of the macromolecules. Also, 4d did not exhibit a T_g because this polymer contained additionally rigid segments derived from perylene dianhydride. In the case of 4e, the reduction of pendant 2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4oxadiazole content due to the introduction of 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole as a comonomer led to a polymer having a T_{q} value of 220 °C. The presence of aromatic ether linkage in the chemical structure decreased the T_g values. Thus, the lower T_g value (201 °C) exhibited the polymer 4b containing both ether and isopropylidene flexible groups. Polymer 4c exhibited a higher *T_g* value (244 °C) because it contained additionally bulky fluorene groups which decreased the flexibility of the macromolecular chains.

The thermal stability was investigated by TGA effectuated under inert atmosphere. Fig. 5 illustrates the TG curves of polymers 4.

All the polymers exhibited high thermal stability, with less significant weight loss up to 440 °C. They lost 5% weight in the range of 445–470 °C, the temperature of 10% weight loss (T_{10}) being in the range of 480–520 °C (Table 1). As can be seen from differential thermogravimetric (DTG) curves, the degradation process exhibited two maxima of decomposition. The first one (T_{max1}) was in the range of 503–554 °C and the second maximum of the decomposition (T_{max2}) was in the range of 577–623 °C (Table 1). The polyimide 4d exhibited



Fig. 6. UV-vis absorption spectra of studied samples: 3 (■), 4a (▼), 4b (♦), 4c (▲), 4d (★) and 4e (●), in DCM solutions. Inset shows zoomed region of 400–550 nm, where appear two weak absorption peaks at 483 and 518 nm originating from perylene moieties.

only one maximum of decomposition at 553 °C. The char yields at 700 °C were in the range of 48.7–61.7%.

3.3. Optical properties

The optical properties of the studied polyimides were investigated in different solvents (in tetrahydrofuran (THF), dichloromethane (DCM), *N*-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) solutions) to analyze the effect of environment. The obtained absorption and emission spectral characteristics are listed in Table 2. Fig. 6 depicts UV–vis absorption spectra of all studied samples in DCM solution. It can be observed that the shape of the absorption spectra of polymers, 4a, 4b and 4c as well as of the copolymers, 4d and 4e, was comparable to that of the corresponding model compound, 3.

These spectra displayed one or two absorption bands depending on the molecular structure of samples and the transparency of the used solvents. Each solvent is transparent (non-absorbing) in a welldefined region of the UV-vis spectrum. For example, in tetrahydrofuran the absorption data were collected in spectral range of 230 to 600 nm and for investigated samples were observed two absorption bands (at cca. 255 nm and 336 nm), instead in NMP solution (where data were collected in spectral range of 270 to 600 nm) one absorption band was obtained. The band at 230–270 nm originates from the aromatic rings inclusive phenylene rings (reported in Table 2 and Fig. 6) in THF and DCM solutions, while the absorption maxima located around 336 nm are attributed to the π - π * transitions involving the phenyl-1,3,4-oxadiazole π -conjugated system. The sample 4c exhibited



Fig. 7. Excitation (a) and emission (b) spectra of studied samples in dimethyl sulfoxide solution, at room temperature.



Fig. 8. Emission spectra of polymer 4d in different media (tetrahydrofuran (THF), dichloromethane (DCM), *N*-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) solutions).

additionally a small absorption peak at 309 nm due to the presence of fluorene moiety. Instead, the copolymer 4d showed additionally two weak absorption peaks situated at 483 and 518 nm in DCM solution, originating from perylene moieties (see inset of Fig. 6).

Fig. 7 shows the excitation and emission spectra of the studied samples in DMSO solution. Excitation spectra were recorded by using the maximum emission wavelength value corresponding to the sample under study. The fluorescence emission spectra of the all studied polyimide derivatives exhibited a broad emission band, excepting for the copolymer 4d, where additionally two weak emission bands appeared at around 530 and 570 nm (attributed to perylene moieties, see Fig. 8 and Table 2) and for copolymer 4e, which showed one poorly resolved shoulder (375 nm), only in DMSO solution (see Fig. 7b). From Fig. 8 we can observe that these two weak emission bands were much better resolved in non-polar solvents (THF and DCM) compared with those



Fig. 9. CIE diagram of polymer 4c in different media.

Table 3

The fluorescence quantum yield (QY, %) values for polymer 4a, in tetrahydrofuran solution, under excitation with different wavelength.

Sample	QY, % at $\lambda_{ex} = 320 \ nm$	QY, % at $\lambda_{ex} = 334 \ nm$	QY, % at $\lambda_{ex} = 350 \ nm$	QY, % at $\lambda_{ex}=360~nm$	QY, % at $\lambda_{ex}=365~nm$	QY, % at $\lambda_{ex}=375~nm$
4a	8.98	8.73	7.43	7.91	6.45	4.23

from NMP and DMSO solvents. Also, from spectral data (Table 2) we observed that the wavelengths of maximum emission of all samples were red shifted depending on the solvent characteristics. The solvent polarity exerted strongly effect (emission spectra showed a remarkable bathochromic shift with increasing solvent polarity, $\Delta\lambda_{max} = 1-55$ nm) on its excited species compared to its ground-state electronic transition (only minor shifts of the absorption band of these compounds occurred from changing the solvent polarity, $\Delta\lambda_{max} = 2-9$ nm). Hence, solvatochromism was more pronounced in the fluorescence spectra. The remarkable shifts of the emission maxima with increasing of the medium polarity reflect the fact that the excited state of investigated molecules is more polar than its ground state and also suggest an increase in dipole moment of excited state compared to ground state. Thus, the solvent (medium) with higher polarity will stabilize the excited state more preferably with respect to the ground state [28].

To obtain detailed information about optical characteristics of studied compounds their fluorescence excitation spectra were measured. Fig. 7 exemplified the excitation spectra of all analyzed samples in DMSO solution. These spectra were characterized by two main bands in the 250–400 nm region. The position of the excitation maxima wavelength of the Band I of the studied samples in all used solvents appeared at around 272 nm. These excitation maxima were shifted to the long wavelength (~272 nm) compared to the first peak from the



Fig. 10. Fluorescence spectra of model compound 3 (a) and polymer 4a (b) in tetrahydrofuran solution, before and after the addition of various amounts of HCl.

absorption spectra (~247 nm, see Table 2) and indicates that the absorbing species of Band I give a weak fluorescence signal. Instead, the second excitation maxima for all samples occurred at wavelength values very close (the small red-shifts to the absorption maxima, $\Delta\lambda_{max} < 6$ nm) to those of the corresponding absorption maxima ones, indicating that the excited emission species can be considered as identical to the absorbing ones [29].

Also, for polyimide 4c, the Fig. 9 illustrates the CIE-1931 chromaticity diagram of this compound in different media. The values of the chromaticity coordinates were represented functions of solvent media. Thus, the emission color changes from THF (x - 0.1523; y - 0.0514, $\lambda_{em} = 419$ nm), DCM (x - 0.1530; y - 0.398, $\lambda_{em} = 414$ nm), NMP (x - 0.1536; y - 0.1752, $\lambda_{em} = 454$ nm) to DMSO (x - 0.1735; y - 0.2420, $\lambda_{em} = 469$ nm).

The calculated Stokes shift values were relatively large, ranging from 80 to 123 nm (3), 81-115 nm (4a), 81-127 nm (4b), 78-126 nm (4c), 79-121 nm (4d) and 79-138 nm (4e) (see Table 2).

Fluorescence quantum yields (QY) of the investigated samples have also been measured in THF and DMSO solutions and the obtained values were summarized in Table 2. The QY values were sensitive to solvent polarity and to excitation wavelength values (Table 3). Thus, the quantum yields of sample 4a in THF decreased with increasing excitation wavelength from 320 to 375 nm (see Table 3). 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. Also, it can be observed that for samples 4b and 4c high quantum yield values were obtained in DMSO (polar solvent) which may be due to the strong overlap of the electronic transitions of species from system [28].

The pH effect on fluorescence characteristics of 3 and 4a samples in THF was investigated by adding various amounts of HCl 1N (Fig. 10). For compound 3 (see Fig. 10a) the maximum of emission intensity from 416 nm was gradually reduced and red shifted to 452 nm after 500 μ L HCl 1 N were added. This red-shift is attributable to protonation of nitrogen atoms from molecular structure of compound 3. In the case of sample 4a, when low amounts of HCl (1–10 μ L, see Fig. 10b) were added, the emission intensity of system was slightly enhanced, probably in this context the effect of heavy-atom was reduced [30], instead further increased HCl concentrations induce a gradual emission quenching and maxima of emission intensity were found red-shifted by \approx 15 nm upon increasing the concentration of HCl. These changes in emission characteristics upon adding acid are due to protonation of the nitrogen atoms from investigated molecular structure.

4. Conclusions

incorporation 2-(4-phenoxy)-5-(4-The of pendant dimethylaminophenyl)-1,3,4-oxadiazole units in the macromolecular chains of some aromatic polyimides containing flexible aromatic ether, isopropylidene, hexafluoroisopropylidene or fluorene groups leads to polymers having high thermal stability and good solubility in organic solvents. The optical properties including UV-visible absorption spectra, fluorescence excitation and emission spectra, Stokes shift values and the relative fluorescence quantum yield were measured in four different solvents. The fluorescence characteristics consist in a blue emission band for all samples, large and solvent dependent Stokes shifts values, as well as solvent dependent quantum yields values. Namely, the fluorescence quantum yield of 4a in THF decreases as the

excitation wavelength changes from 320 nm to 375 nm. The emission intensity of samples 3 and 4a in THF solution was quenched and red-shifted in the presence of a protonic acid (HCl 1N).

Acknowledgements

The financial support of MEN-UEFISCDI through PN-II-PT-PCCA-2013-4-1861 project, Partnership in S&T priority domains, contract no. 272/2014, is gratefully acknowledged.

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