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Copolymer architectures containing donor and acceptor units for blue light-emitting diodes

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Here we describe a study of the properties of some polyoxadiazoles containing bulky fluorene units suitable for blue polymer light emitting diodes (LEDs). These copolymers present good solubility in convenient solvents such as NMP, DMF, DMAc and THF, allowing to obtain thin films by pouring the solutions of polymers onto glass substrates or silicon wafers. Very thin films as-deposited onto glass plates studied by AFM technique exhibit a free pinhole, very smooth surface and practically without defects, over a scanning range of 3 - 10 μm. All the copolymers show good thermal stability, up to 400 °C and glass transition temperature in the range of 144-173 °C. UV-vis absorption spectra of these polymers performed in very dilute solutions exhibit absorption peaks and shoulders in the range of 280 - 340 nm. Excited with UV light peaking at 360 nm, the polymers in solutions and in solid state show photoluminescence in the blue domain.

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1. Introduction

Fully aromatic poly(1,3,4-oxadiazole)s form a class of high performance polymers that are designed for use in small quantities, but with very high end-value [1,2]. High performances include electronic properties, electric conduction, optical properties, good hydrolytic stability, highly ordered systems, mechanical resistance and high thermal stability. There is currently much research directed towards the discovery of new blue light-emitting polymers, with characteristics of high efficiency and high reliability. For such a purpose polyoxadiazoles are of great interest because, due to the electron-withdrawing character of the 1,3,4-oxadiazole rings, they can facilitate the injection and transport of electrons. On the other hand, polyfluorenes were introduced as a prospective emitting layer for polymer LEDs. These materials are thermally stable and display high photoluminescence (PL) efficiencies both in solution and in solid films with emission wavelengths primarily in the blue spectral region. Their photostability and thermal resistance are better than those of the poly(phenylene vinylene)s, which are among widely studied polymers for LEDs. Polyfluorenes contain a rigidly planarized biphenyl structure in the fluorene repeating unit, while the remote substitution at C-9 produces less steric interaction in the conjugated backbone itself than in comparison with poly(p-phenylene)s [3-5]. The insertion of electron transporting groups in *p*-type polymers enhances bipolar carrier transport ability. The combination of donor-acceptor groups in the same chain in attempts to achieve balanced electron–hole injection and transport, avoiding the use of intermediate transport layers, has been widely explored. Such combination in the same chain can be oxadiazole with oligothiophenes, naphthalimide, fluorene, anthracene or triphenyl amine [6]. Therefore, we considered interesting to make polymers containing both oxadiazole rings and fluorene units. Here we present a study of the properties of some polyoxadiazoles containing silicon placed among aromatic neighbours in the main chain, able to support the transport of electrons along the macromolecular chain through σ-π conjugation [7,8], and bulky fluorene units pendent to the chain, suitable for polymer blue light-emitting diodes (LEDs).

2. Experimental

Monomers

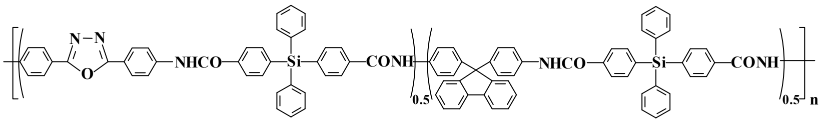
2,5-Bis(p-aminophenyl)-1,3,4-oxadiazole, 2,5-bis[4-(p-aminophenoxy)-phenylene]-1,3,4-oxadiazole and 2,5-bis[3-(p-aminophenoxy)-phenylene]-1,3,4-oxadiazole were prepared according to published procedures [9-11].

Aromatic diamine containing fluorene unit, namely *9,9-bis(p-aminophenyl)-fluorene*, has been purchased from Aldrich and recrystallized from a mixture of ethanol and water. M.p. 241-243°C.

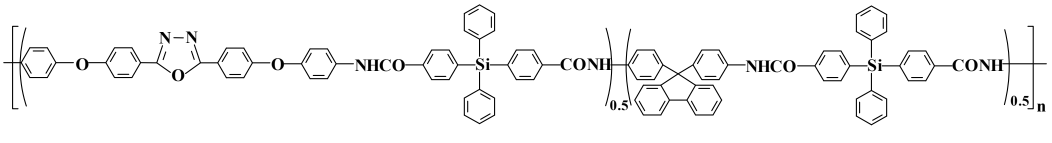
The silicon-containing diacid chloride, namely *bis(p-chlorocarbonyl-phenylene)-diphenylsilane,* was prepared by a published multi-step reaction [12].

Polymers

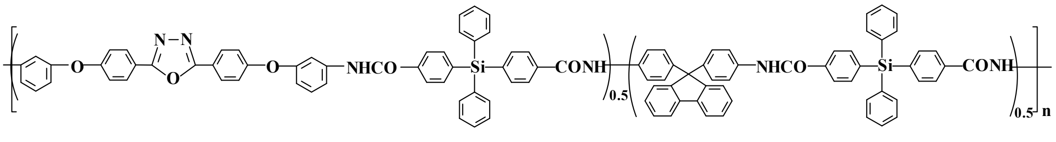
The copolymers **Ia-c** have been prepared by low-temperature polycondensation reaction of silicon-containing diacid chloride with a mixture 1:1 of a diamino-oxadiazole with the diamine containing fluorene unit, using NMP as a solvent and with pyridine as an acid acceptor. The relative amounts of monomers and NMP were adjusted as to have a solid content of 10-18 %. The structures of these polymers are shown in Fig. 1.



Ia



Ib



Ic

Fig. 1. Structures of the polymers.

Polymer films

1 g of polymer was dissolved in 10 mL NMP. Half of the solution was cast onto glass plates and dried in an oven at 100, 130, 160, 190 and 210°C for 30 min each. The obtained films were brittle. The other part of polymer solution was diluted with NMP to 1-1.5 % concentration and it was used to cast very thin films having the thickness in the range of nanometers, onto glass plates by a spin-coating technique, at a speed of 5000 rotation/min. These films, as deposited, were gradually heated to 210°C in the same way as described earlier to remove the solvent and they were used for atomic force microscopy (AFM) investigations.

Measurements

The inherent viscosities of the copolymers were determined at 20°C, by using NMP-polymer solutions of 0.5 g/dL concentration, with an Ubbelohde viscometer.

The infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using KBr pellets.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 7.5. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles).

The quality of very thin films as-deposited on glass plates was investigated by atomic force microscopy (AFM) using a Scanning Probe Microscopy Solver PRO-M, NT-MDT equipment made in Russia, in the semi-contact mode, semi-contact topography technique.

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) using a Mettler 681e Instrument operating at a heating rate of 10 °C /min, in nitrogen. The temperature corresponding to the onset on the TG curve was regarded as the initial decomposition temperature (IDT). The temperature of maximum rate of decomposition which is the maximum signal in differential thermogravimetry (DTG) curves was also recorded.

The glass transition temperature (T_g) of the polymers was recorded on a Diamond DSC Perkin Elmer apparatus. Approximately 3 to 8 mg of each polymer were crimped in aluminium pans and run in nitrogen with a heat-cool-heat profile from room temperature to 380°C at 10°C/min. The mid-point temperature of the change in slope of the DSC signal of the second heating cycle was used to determine the glass transition temperature of the polymers.

The UV-Vis absorption and photoluminescence spectra of the copolymers were registered with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, by using very diluted polymer solutions in DMAc or very thin films cast from 1 % solution of polymers in THF.

3. Results and discussion

Copolymers **I** having the structure shown in scheme 1 have been prepared by low-temperature polycondensation reaction of a diacid chloride containing diphenylsilylene unit with a mixture 1:1 of diamino-oxadiazoles with 9,9-bis(p-aminophenyl)-fluorene. The structure of these polymers was identified by FTIR spectra. All the spectra exhibited characteristic absorption bands at 3375-3423 cm^{-1} (wide) due to NH and at 1687 - 1690 cm^{-1} due to CO in amide groups. The oxadiazole ring was evidenced by absorption peaks at 1018 -1019 cm^{-1} and 953 -961 cm^{-1} which were also present in the spectra of the diamino-oxadiazole monomers. The broad absorption peaks at 3015 - 3066 cm^{-1} were attributed to C-H aromatic bonds, while the strong absorption peaks from 1485-1500 and 1597-1600 cm-1 were assigned to aromatic C=C bonds. Characteristic absorption bands for phenyl-silane bonds were found at 1427 - 1428 cm^{-1}, 1106 - 1107 cm^{-1} and 697 - 708 cm^{-1}.

The inherent viscosities of these copolymers were in the range of 0.12-0.18 dL/g. All the polymers were easily soluble in polar amidic solvents such as N-methylpyrrolidone (NMP), dimhetylformamide (DMF) and dimhetylacetamide (DMAc) and even in less polar liquids, like pyridine or tetrahydrofurane (THF). The improved solubility of these polymers compared with conventional poly(arylene-oxadiazole)s, which are only soluble in strong acids such as H_2SO_4 and methansulfonic acid, can be explained by the presence of flexible amide groups and voluminous phenyl substituents, and the bending of the chains at silicon atoms which make the shape of the macromolecule to be far from a “rigid-rod”, and thus facilitate the diffusion of the small molecules of solvent. The better solubility of these copolymers compared to related polyamides without fluorene units [10] was explained by the presence of bulky fluorene groups in the side chains which increase the free volume of the polymers and thus allow the solvent to penetrate among the polymer chains. The shapes of the copolymer chains can be visualized by molecular modelling, as shown in Fig. 1.

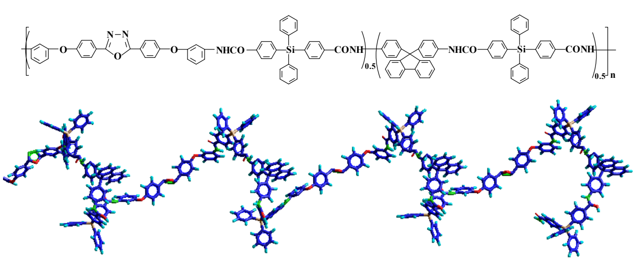


*Fig. 1. Model of a fragments incorporating four repeating units of the polymer **Ic**.*

The good solubility makes the present polymers potential candidates for practical applications in spin-coating and casting processes. All these polymers possess film forming ability. The polymer solutions (10 %) in NMP were processed into thin films by casting onto glass plates. The free-standing films prepared from these copolymers having a thickness in the range of 5-30 μm were brittle. Very thin films having the thickness in the nanometer range were deposited by spin-coating technique onto glass plates, by using diluted polymer solutions (1 %). The quality of these films as-deposited onto glass plates was studied by atomic force microscopy (AFM) (figure 2). All the films prepared from the copolymers **I** exhibited a very good quality: smooth surface without peaks or pinholes, practically without defects, over a scanning range of 3 - 10 μm. The root mean square roughness was in the range of 5-10 Å, close to that of the substrate.

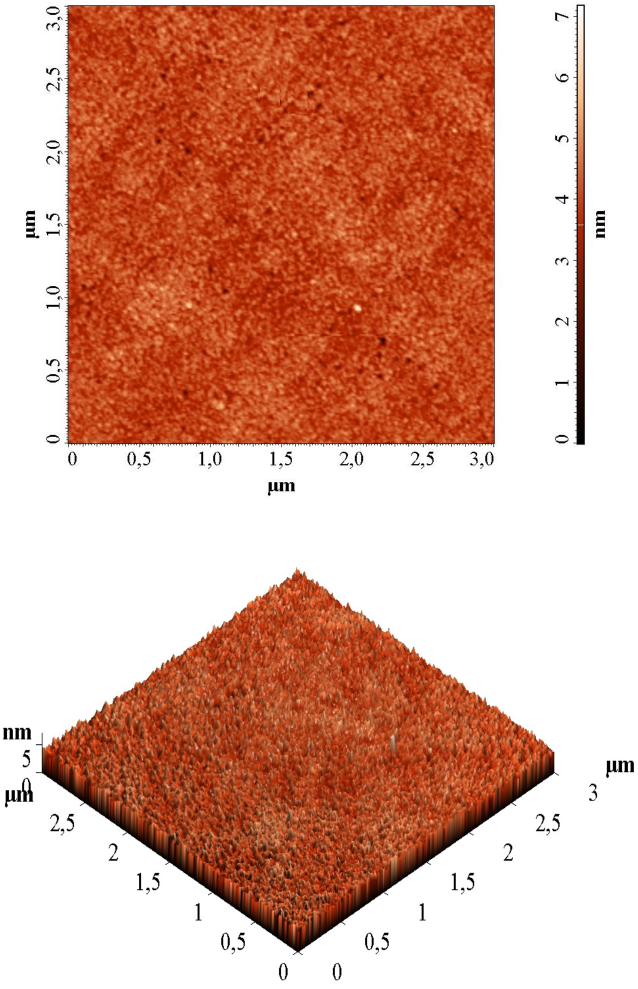


*Fig. 2. AFM image of the copolymer **Ib**.*

The polymers are highly thermostable, with initial decomposition temperature (IDT) being above 395 °C (Table 1), as evaluated by thermogravimetric analysis. These copolymers start their decomposition at 398 - 447 °C. The temperature of the maximum decomposition rate (T_{max}) as evidenced by DTG curves is above 425 °C. The values of decomposition temperatures (table 1) showed that there is no significant difference in the thermal behaviour of these copolymers and related polymers without fluorene units [13]. They all have high thermal stability, similar to that of previously reported polyoxadiazole-amides without flexible diphenyl-silane groups [12]. All these data demonstrate that incorporation of fluorene pendent units into the backbone effectively enhances the solubility while maintaining a very good thermal stability. Representative TG and DTG curves are shown in Fig. 3.

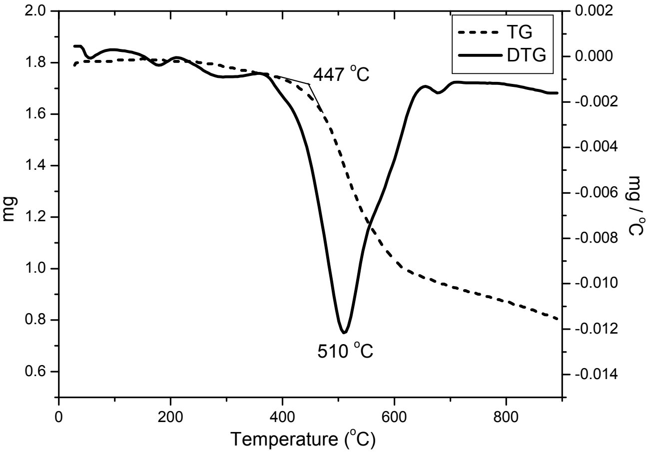


*Fig. 3. TG and DTG curves of copolymer **Ia**.*

The glass transition temperatures (T_g) of these copolyoxadiazoles were measured by differential scanning calorimetry. The values of T_g are in range of 144 - 173 °C (table 1), being with approximately 100 °C lower than that of related polyoxadiazoles without fluorene units [10]. Such behaviour could be attributed to the higher free volume determined by the presence of pendent bulky fluorene units. The large interval between decomposition and glass transition (over 200 °C) may be useful for the processing of these polymers by a thermoforming technique, as well. Moreover, these copolymers present melting points between 212 and 248 °C, as compared with related polyoxadiazoles [13] that do not melt before decomposition. This means that the present copolymers could be also processed from the molten state. More important, in the second heating in DSC experiment they do not present melting which means that they do not recrystallize by cooling. Typical DSC curves are shown in Fig. 4.

Table 1. Thermal properties of the polymers.

Polymer	T_g (°C)	*IDT (°C)	$^{**}T_{max}$ (°C)
Ia	173	447	509
Ib	144	406	460
Ic	157	398	428

T_g = glass transition temperature
IDT = onset on the TG curve
T_{max} = temperature of the maximum rate of decomposition

There is currently much interest in polymeric electroluminescent materials, particularly those which are able to emit blue light that is difficult to be attained with the already known inorganic ones [14].

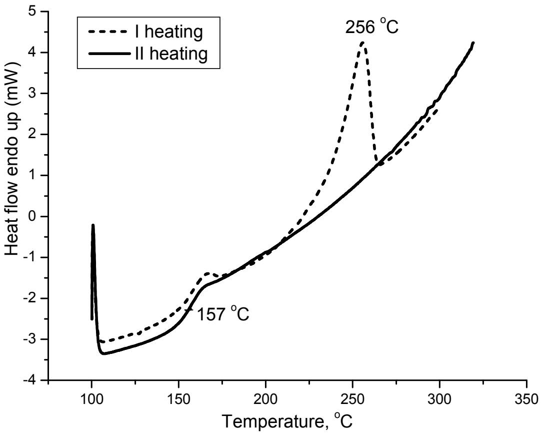


*Fig. 4. DSC curves of copolymer **Ic**.*

In addition, the use of electroluminescent thin films made from highly thermostable polymers would avoid the thermal degradation in the final device while in service at elevated temperatures. Since during the formation of polymeric thin films, by spin coating or dip-coating, pinholes are likely to form and therefore will cause the electroluminescent device to break during its operation, there is a strong requirement that electroluminescent polymers should have an outstanding capability to form pin hole-free films, with a strong adhesion to various substrates. Therefore, the light emitting properties of these silicon-containing copolymers have been investigated. The light emitting ability of these polymers containing both oxadiazole and fluorene units was evaluated on the basis of photoluminescence spectra which were recorded for polymer solution in N,N-dimethylacetamide or for films cast from THF solutions, after irradiation with UV light peaking at 360 nm. The UV absorption spectra of these copolymers in solution showed maxima and shoulders in the range of 280 - 340 nm which are determined by the π - π* transitions in the isolated polymer molecules. In figure 5, the absorption spectra of the three copolymers in DMAc solution are reported.

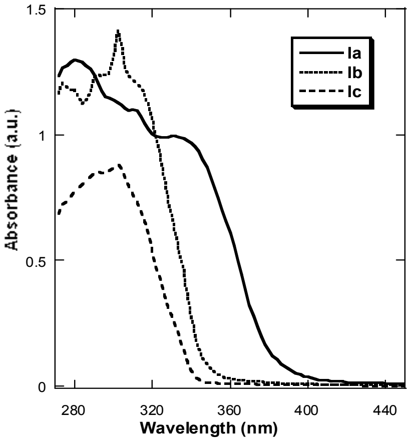


*Fig. 5. UV absorption spectra of copolymers **I**.*

Excited with UV light peaking at 360 nm, the polymers **Ia**, **Ib** and **Ic** showed blue photoluminescence (PL), with maximum emission peak at 403, 431 and 428 nm, respectively, in DMAc solution. Copolymers **IIb** and **IIc** presented a red shift of the emission maxima compared with copolymer **Ia**, probably due to the substitution of phenylene rings with oxygen: in the excited state the oxygen acts as a better bridge for the delocalisation of the charge, because the position of the phenylene ring next to the oxygen determines the PL more significantly [10]. The photoluminescence maximum of the copolymers films cast from THF solutions ranged between 414 and 430 nm. The red shift of PL maximum in film (430 nm) compared with solution (403 nm) of the copolymer **Ia** which do not contain oxygen bridges could be explained by negligible intermolecular interactions of the conjugated parts of the polymer chains. The films of copolymers **Ib** and **Ic** showed PL maximum at 414 nm, being blue shifted compared with solutions. This behaviour could be explained by the fact that polymers containing fluorene could have different aggregation amount and form excimers in films which could result in fluorescence quenching, enlargement of the emission bands and bathochromic effect [15]. The photoluminescence spectra of the copolymers in solution and films are shown in Fig. 6.

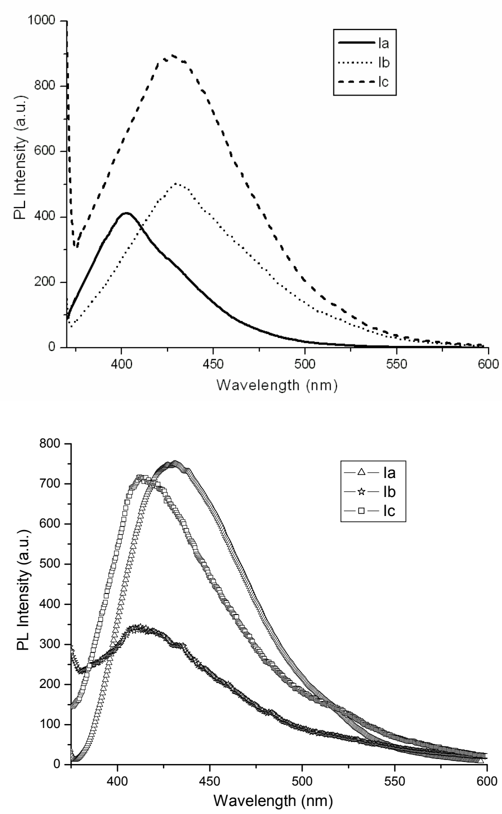


Fig. 6. Photoluminescence spectra of the copolymers (top: in solution, down: in films).

4. Conclusions

Silicon-containing heterocyclic copolymers have been synthesized by solution polycondensation of a diacid chloride incorporating diphenylsilane linkage with a mixture of aromatic diamines containing oxadiazole and fluorene units. They show high thermal stability, with decomposition starting at about 400 °C and a glass transition in the range of 144 - 173 °C. The polymers are soluble in polar solvents and in less polar solvents and can be processed into very thin films from such solutions. These very thin films with thickness in the range of nanometers are pinhole-free, compact and homogeneous, practically without defects. They showed blue photoluminescence in solution and films, with a maximum in the range of 403-430 nm, indicating their promise as candidates for future use in LEDs. Potential applications in optoelectronics, microelectronics, or other related advanced fields are foreseen.

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