



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

FLUORINATED HETEROCYCLIC POLYPERYLENEIMIDES

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New polyperyleneimides containing 1,3,4-oxadiazole rings and hexafluoroisopropylidene linkages were synthesized by solution polycondensation reaction at high temperature of aromatic diamines having oxadiazole rings with a mixture of perylenetetracarboxylic dianhydride and hexafluoroisopropylidene diphthalic dianhydride. The solubility and thermal stability of these polymers were studied and compared with those of related polyimides and polyoxadiazoles. The film-forming ability and the quality of the resulting thin films were investigated by using atom force microscopy and scanning electron microscopy, which showed that the films were organized into self-assembled rod-like structures. The photoluminescence of the polymers, both in solution and in solid state, after irradiation with light of different wavelengths, were also studied.

INTRODUCTION

The increasing demand of advanced technologies for new materials offering high thermal, chemical and mechanical resistance and other special properties as electron-transporting ability, electroluminescence, optical and electrical conductivity and other electrophysical characteristics stimulates the growing interest in aromatic polymers containing heterocyclic units.¹⁻³ Among these polymers, aromatic polyimides achieved a good combination of various properties which makes them appropriate for a variety of high performance applications. For particular application in electroluminescent devices, a combination of electrono-donor and electrono-acceptor units into the same macromolecular chain is expected to provide a good transport of electrons, hence a high efficiency of light-emission.

Therefore, the inclusion of imide rings together with other electron-rich rings, such as perylene, and with electron-withdrawing units, such as 1,3,4-

oxadiazole, could be a good way to obtain light-emitting polymers having a desired balance of properties.

The introduction of perylene units into a polyimide chain can be achieved by using the dianhydride of perylenetetracarboxylic acid as a monomer in the polycondensation reaction with various diamines. But the polyperyleneimides reported so far exhibited very low molecular weight and very poor solubility in organic solvents. This was explained by the low reactivity of perylenetetracarboxylic dianhydride determined by the lack of strain of six-membered anhydride ring.⁴ The use of a more reactive dianhydride, such as hexafluoroisopropylidene diphthalic dianhydride together with perylenetetracarboxylic dianhydride could lead to an increase of the molecular weight of the resulting polyimides and enhance the solubility due to the flexible hexafluoroisopropylidene linkages. Frequently, the inclusion of hexafluoroisopropylidene into the polymer

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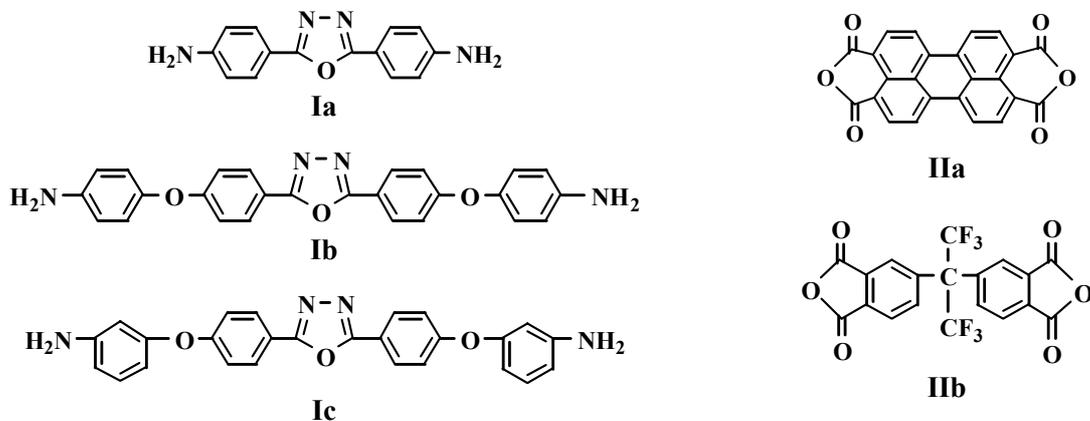
structure will increase the thermal stability, flame retardancy, oxidation resistance, transparency and environmental stability, while there is often a decrease in colour, crystallinity, surface energy and water absorption. The bulky hexafluoroisopropylidene groups also serve to increase the free volume of the polymers, thus improving its electrical insulating characteristics.^{5,6} On the other hand, the introduction of a kink into rigid polyimide chain, by using the oxadiazole ring, could also be beneficial for the solubility. Besides, aromatic polyoxadiazoles are also known for their superior thermal stability and other high performance properties due to the following factors: the oxadiazole ring does not contain any hydrogen atoms, from the spectral and electronic points of view it is similar to a *p*-phenylene structure which is known to be thermoresistant, it lacks tension, it doesn't have any possibilities of rearrangements, it has structural symmetry, and it is thermally unreactive. Poly(1,3,4-oxadiazole)s are of great interest for electroluminescent devices due to electron-withdrawing character of the 1,3,4-oxadiazole ring that can facilitate the injection and transport of electrons.⁷⁻⁹

Here we present the synthesis of a series of polyperyleneimides containing oxadiazole rings and hexafluoroisopropylidene linkages, and the study of their solubility, thermal stability, glass transition, film-forming ability and photoluminescence of their films and solutions.

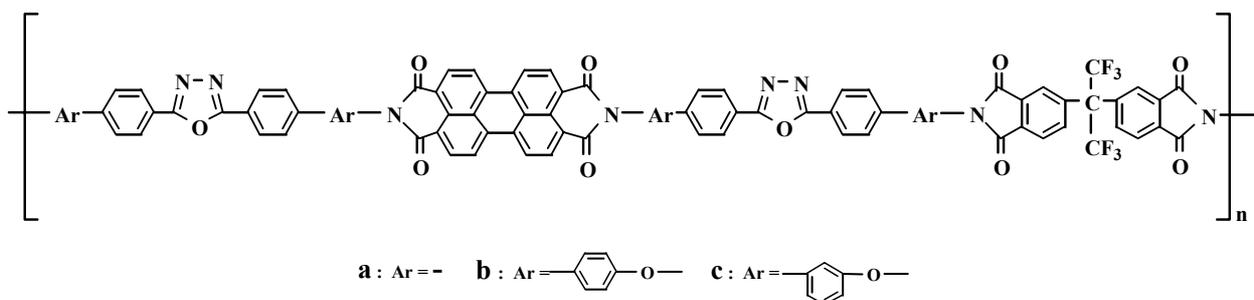
RESULTS AND DISCUSSION

Three aromatic diamines containing oxadiazole rings, **I**, and two aromatic dianhydrides, **II**, one of them containing perylene condensed ring and another one having hexafluoroisopropylidene groups, whose structures are shown in Scheme 1 were used for the synthesis of the present fluorinated polyperyleneimides containing oxadiazole rings **III**.

The polycondensation of a diamine with a mixture 1:2 of perylene dianhydride, **IIa**, and fluorinated dianhydride, **IIb**, was run in NMP + 5% LiCl at 200°C to give the polymers **III** whose structures are shown in Scheme 2. The overall molecular ratio between diamine and dianhydride mixture was 1:1 and the total concentration of monomers in solution was 8%.



Scheme 1 – Structures of monomers, **I** and **II**.



Scheme 2 – Structures of fluorinated polyperyleneimides containing oxadiazole rings, **III**.

Attempts have been made to increase the amount of perylene dianhydride, **II**, but the resulting polyimides precipitated during reaction at high temperature and they did not redissolve by further heating, nor by dilution.

The structures of the resulting polymers were identified by infrared spectroscopy (FTIR). All the polymers exhibited strong absorption bands characteristic for imide rings in the range of 1770-1780 cm^{-1} (asymmetrical C=O imide stretching), 1720-1730 cm^{-1} (symmetrical C=O imide

stretching) and 720-730 cm^{-1} (imide ring deformation) and weak IR absorption peaks characteristic for 1,3,4-oxadiazole rings in the range of 960-970 cm^{-1} and 1010-1020 cm^{-1} (=C-O-C= stretching). C-F showed absorption peak in the range of 1100-1300 cm^{-1} . The polymers **IIIb** and **IIIc** also showed strong absorption bands at 1240-1250 cm^{-1} which is characteristic of aromatic ether stretching. A typical FTIR spectrum is shown in Figure 1.

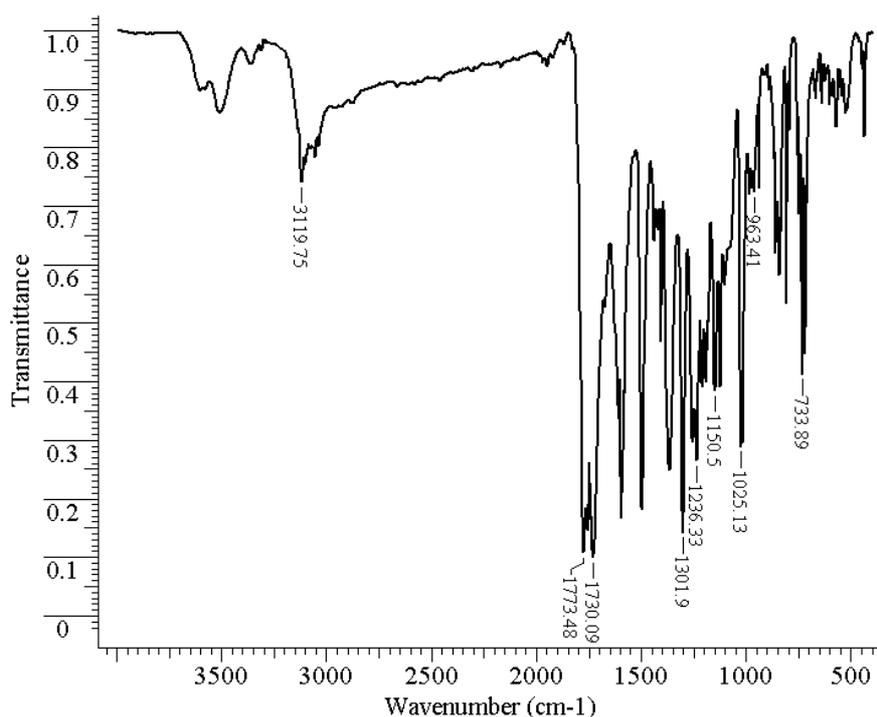


Fig. 1 – FTIR spectrum of the polymer **IIIa**.

It is known that conventional aromatic polyperyleneimides are insoluble in easy accessible and safe organic solvents, being soluble only in *m*-cresol, due to the rigid nature of perylenediimide unit which dictates the overall shape of the corresponding macromolecules and thus facilitates the strong interchain interactions and due to the compact aggregation of the polymer chains which occurs during imidization that is carried out at high temperatures¹⁰. Our fluorinated polyperyleneimides containing oxadiazole rings are soluble in a convenient aprotic amidic solvent which is NMP, at a concentration of 0.5-1% due to the presence of flexible hexafluoroisopropylidene linkages and oxadiazole rings in the macromolecular structure that leads to a higher solubility compared with their analogues without hexafluoroisopropylidene and oxadiazole units.

Oxadiazole rings and flexible ether or hexafluoroisopropylidene introduce a deviation from the linearity of the chain and disturb the tight packing of the polymer chains and make the shape of the respective macromolecules to be far from a linear rigid rod which is characteristic to aromatic polyimides based only on perylene tetracarboxylic acid dianhydride.

The inherent viscosity values of these polymers **III** were in the range of 0.15-0.25 dL/g. These relatively low values of viscosity show that the introduction of rigid perylene moieties into polyimides hampers the formation of products with high viscosity, as shown by literature data, as well.^{11,12}

The thermal stability of the present polymers was evaluated by thermogravimetric analysis which showed that they did not decompose up to

470°C; the temperature of 10% weight loss was in the range of 480-510°C and the temperature of the maximum decomposition rate as evidenced by DTG curves was above 530°C (Table 1). All these data show that these polymers have high thermal stability, similar to that of other polyimides based on the same perylenetetracarboxylic dianhydride but without oxadiazole rings¹³ and other related polyperyleneimides which do not contain

hexafluoroisopropylidene linkages.⁴ Thus, the thermal stability of the present polyimides is not affected by the introduction of flexible hexafluoroisopropylidene unit in the main chain, nor of 1,3,4-oxadiazole ring, while the solubility and the film-forming ability of the resulting polymers are much improved due to the presence of these units.

Table 1

Thermal properties of the polymers **III**

Polymer	IDT (°C)	T ₁₀ (°C)	T _{max} (°C)	T _g (°C)
IIIa	480	485	535	282
IIIb	475	480	530	267
IIIc	470	510	550	227

IDT = temperature of 5% weight loss; T₁₀ = temperature of 10% weight loss;

T_{max} = temperature of maximum decomposition rate; T_g = glass transition temperature

These polymers do exhibit a glass transition, although high, as evidenced by differential scanning calorimetry, in contrast with fully aromatic polyimides and aromatic polyoxadiazoles that do not have any glass transition or their glass transition is in the same range with their decomposition. The values of T_g of the present polymers are in the range of 227-282°C with a large interval, of about 200°C, between T_g and decomposition temperature, which could be advantageous for their processing by a thermoforming technique. It is clear that the presence of hexafluoroisopropylidene groups renders some flexibility to the macromolecular chain.

All these polymers possess film-forming ability as shown by casting 8% polymer solution onto

glass plates. The free-standing films having a thickness of 40-50 μm, were flexible, tough, and maintained their integrity after repeated bendings. These films had a very strong adhesion to the support and they could be only taken off the plates by boiling in water.

Very thin films having the thickness in the range of tens of nanometers were deposited by spin-coating technique onto silicon wafers, by using diluted solutions (concentration of 1%). The quality of these thin films was examined by atom force microscopy (AFM). These spin-coated films are smooth, homogeneous, without cracks or pinholes, and are self-organized into vertically segregated structures. Typical AFM images are shown in Figure 2.

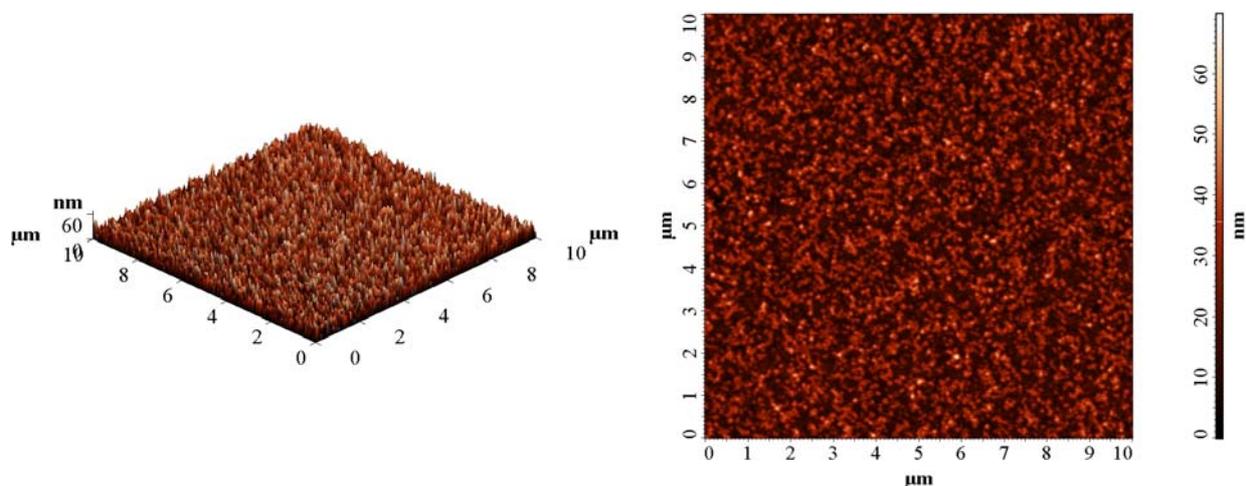


Fig. 2 – AFM images (left: side-view, right: top-view) of a film made from polymer **IIIc**.

It is presumed that the polymer chains are strongly packed in solid-state similar to other polyimides.¹⁴ The morphology of the resulting supramolecular assembly was reflected in scanning electron microscopy (SEM) images. SEM images of the free-standing films of these polymers show that they are organized into self-assembled well-ordered building blocks that form supramolecular rod-like structures which tend further to aggregate in bigger rods. These aggregates are mainly determined by the π - π stacking interactions of perylenediimide units.

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.¹⁵ 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. Since 1,3,4-oxadiazole rings and perylenediimide units are known as light-emissive,^{16,17} the light-emitting properties of these fluorinated polyperyleneimides having oxadiazole rings were investigated. The light-emitting ability of these polymers was assessed on the basis of photoluminescence spectra

which were recorded for both polymer solutions and polymer films, after excitation with light of different wavelengths.

The dominant aspect in these materials is their extended conjugated π -system; such extension is mirrored by the electronic absorption spectrum. Figure 3 shows the absorption spectra of polymer **IIIc** as solution and film. It was found that all these oxadiazole-containing polyperyleneimides in solution show one strong UV absorption maximum at 303-304 nm, and two peaks at 492-493 nm and 526-529 nm, the spectra being quite identical (Table 2). A weak absorption shoulder at about 375 nm in the UV spectra of polymers **IIIb** and **IIIc** was detected, as well. The absorption maxima at 303-304 nm of these polyimides are mainly determined by the diphenyl-1,3,4-oxadiazole unit, because the unsubstituted diphenyl-1,3,4-oxadiazole in hexane shows its absorption maximum at 284 nm.¹⁸ The absorption peaks at 492-493 nm and 526-529 nm are due to the chain segments containing perylenediimide units and are lower in intensity as compared with the absorption bands characteristic of diphenyl-1,3,4-oxadiazole unit.¹⁶

The films made from these polymers exhibited two absorption maxima in the range of 494-501 nm and 531-539 nm. The polymers **IIIb** and **IIIc** containing ether bridges in their repeating units, showed an additional weak absorption shoulder at 373-375 nm, which was attributed to spin-allowed π - π^* transitions involving the imide-phenyl framework.

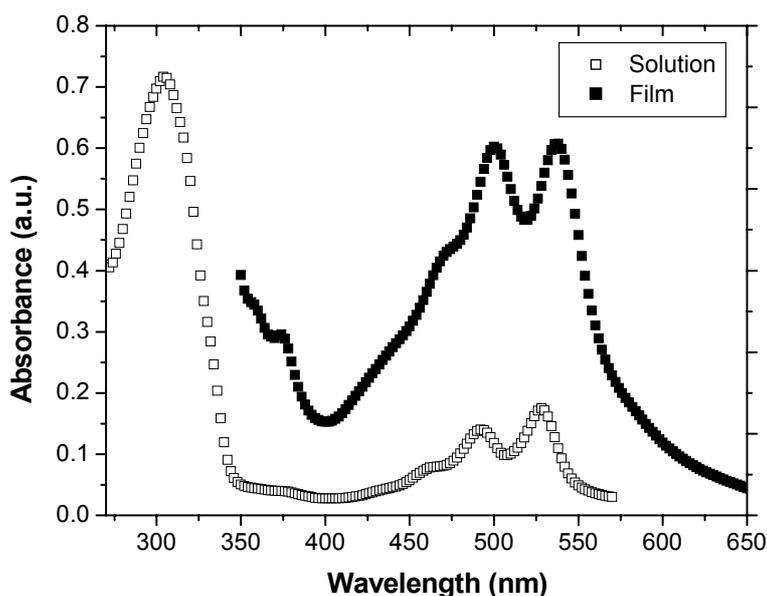


Fig. 3 – UV-vis absorption spectra of polymer **IIIc** in solution and solid state.

The absorbance spectra of solutions and thin films allow us to compare the position of absorption bands λ_{abs} , as seen in Table 2. The small red-shift (2-10 nm) of the absorption maxima from the highest wavelength characteristic to perylenediimide units in solid state with respect to solution could be explained by the fact that the surrounding chromophore polarity became weaker,

and the intermolecular interaction of the polymer backbones became stronger.

The photoluminescence of these polymers was evaluated after irradiation of their solutions and films with light with different wavelengths. The values of maximum wavelengths of emission are given in Table 3.

Table 2

UV absorption maxima of the polymers **III**

Polymer	λ_{max} solution (nm)	λ_{max} film (nm)
IIIa	303, 492, 526	494, 531
IIIb	304, 376 ^s , 493, 529	375 ^s , 499, 537
IIIc	304, 375 ^s , 492, 529	373, 501, 539

λ_{max} - wavelength of the maximum absorption peak; ^s - shoulder.

Table 3

Photoluminescence properties of the polymers **III**

Polymer	λ_{em} (nm) after irradiation at 303-304 nm	λ_{em} (nm) after irradiation at 360 nm	λ_{em} (nm) after irradiation at 492-493 nm
IIIa	406, 537, 578	406, 534, 577 ^s	536, 578 ^s
IIIb	368, 538, 577	407, 443, 538, 577	537, 577
IIIc	370, 536, 580	407, 438, 536, 577	538, 579

λ_{em} - wavelength of the maximum emission peak

Since the absorption spectra present characteristic absorption for each individual chromophore, and even for conjugated parts containing these chromophores or imide rings, we investigated the photoluminescence (PL) ability of these polymers by exciting with light of different wavelengths. Thus, by exciting at the maximum absorption wavelengths (303-304 nm) characteristic to diphenyl-1,3,4-oxadiazole chromophore and at 360 nm, polymer **IIIa** displayed similar spectra with one strong and large emission band centered around 406 nm, in the blue domain, due to the emission of oxadiazole, imide and phenylene rings, and two maxima in the green and yellow spectral range, around 537 nm and 578 nm, respectively, due to the emission of perylenediimide moieties (Figure 4).

When excited with light of 303-304 nm, polyimides **IIIb** and **IIIc** exhibited one broad weak emission maximum in the UV domain, centered at 368-370 nm, and two peaks within 536-538 nm and 577-580 nm range. When the excitation was done with light of 360 nm (Table 3) the bands from UV domain of these two polymers are splitted and red-shifted to 407 nm and 438-443 nm (blue domain).

For comparison, a related polyperyleneimide which did not contain oxadiazole rings, based on the same mixture of dianhydrides, but with diamino-diphenyl-ether,¹⁹ was also irradiated with UV light of 360 nm. The resulting PL spectrum exhibited two maxima in the blue domain, at 408 and 442 nm, and another two emission maxima in the green and yellow range, at 538 and 577 nm, respectively. This shows that the PL emission that shifted from UV-domain to blue region is mainly determined by segments containing imide rings having different conjugation length, and not by the diphenyl-oxadiazole chromophore. The PL spectra of all polymers also show a strong emission of perylenediimide moieties, while the emission of oxadiazole moieties is completely quenched in case of polyimides **IIIb** and **IIIc**. Because the absorption maximum of diphenyl-oxadiazole chromophore is at 304-306 nm and the perylenediimide moieties did not directly absorb these wavelengths light, an excitation energy transfer from oxadiazole to perylenediimide moieties must have taken place for which the oxygen bridge appear to be responsible. A similar effect was previously noted by other authors.¹⁶ It appears that in the excited state, the oxygen acts as

a better bridge for the delocalization of the charge, because the position of the phenylene ring next to the oxygen determines the PL more significantly in the case of polymers **IIIb**, **IIIc** and related polyperyleneimides containing ether bridges but

without oxadiazole rings. The emission spectra of polyperyleneimides excited by light of 492-493 nm, showed two peaks at 536-538 nm and 577-579 nm, which corresponded to the emission of perylenediimide moieties (Table 3).

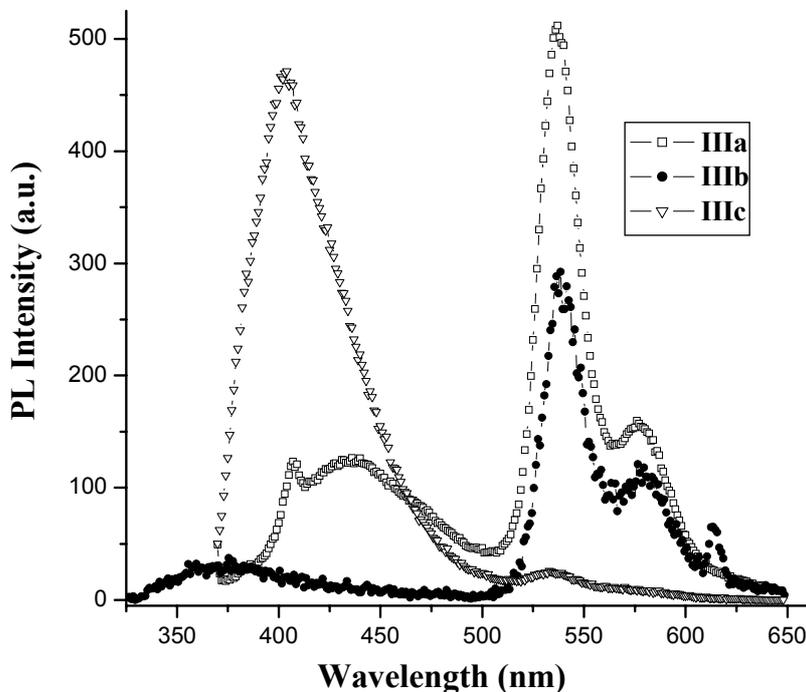


Fig. 4 – PL spectra of the polymers **III** after excitation with UV light of 360 nm.

No emission was observed in solid state. This is probably due to the high content of perylenediimide chromophore which leads to fluorescence quenching through aggregation.

EXPERIMENTAL

Monomers

2,5-Bis(*p*-aminophenyl)-1,3,4-oxadiazole, **Ia**, was prepared by the reaction of *p*-aminobenzoic acid with hydrazine hydrate in polyphosphoric acid, according to a published procedure.²⁰ Mp = 260-262°C.

2,5-Bis[4-(*p*-aminophenoxy)phenylene]-1,3,4-oxadiazole, **Ib**, and 2,5-bis[4-(*m*-aminophenoxy)phenylene]-1,3,4-oxadiazole, **Ic**, whose structures are shown in Scheme 1, were synthesized by a known procedure starting from 4-fluorobenzoic acid and hydrazine hydrate which first reacted in PPA to give 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole, followed by the reaction of the latter with *p*- or *m*-aminophenol in 1-methyl-2-pyrrolidinone (NMP) as solvent and in the presence of K₂CO₃.²¹ Mp **Ib** = 225-227°C, **Ic** = 188-190°C.

3,4,9,10-Perylenetetracarboxylic dianhydride was purchased from Aldrich and purified following a procedure described in the literature.²² 4,4'-(Hexafluoroisopropylidene)-diphthalic dianhydride was purchased from Aldrich and purified by recrystallization from a mixture of glacial acetic acid and acetic anhydride, followed by thoroughly washing with anhydrous diethyl ether.

Synthesis of the polymers

The polymers **III** have been prepared by one-step polycondensation reaction of oxadiazole-containing diamines, **I**, with a mixture 1:2 of 3,4,9,10-perylenetetracarboxylic dianhydride, **IIa**, and 4,4'-(hexafluoroisopropylidene)-diphthalic dianhydride, **IIb**. The overall ratio of diamine : dianhydride mixture was 1:1. The reactions were carried out in NMP + 5% LiCl, at a concentration of 8% total solids, under nitrogen stream, at high temperatures (200°C), for 10 h. The generated water of imidization was removed through a slow stream of nitrogen.

The following example illustrates the general procedure. In a 100 mL three-necked, round-bottomed flask equipped with a mechanical stirrer and nitrogen inlet and outlet were introduced 1.512 g (0.006 mol) of diamine **Ia** and 26 mL of NMP + 5% LiCl, as solvent. After complete solubilization of the diamine, 1.176 g (0.003 mol) of perylenetetracarboxylic dianhydride was charged. The reaction mixture was stirred and purged with a slow nitrogen stream for about half an hour and then 1.334 g (0.003 mol) of hexafluoroisopropylidene-diphthalic dianhydride and 20 mL of NMP + 5% LiCl were added. The reaction mixture was stirred and heated to 200°C and allowed to react for 10 h, then gradually cooled to room temperature. Part of the resulting dark red polyimide solution was poured onto glass plates in order to prepare thin films, while the rest was poured into water to precipitate the solid polymer. The dark red polymer was washed with plenty of water and finally treated with ethanol in a Soxhlet apparatus for 1 day in order to remove the unreacted monomers and the high boiling solvent. Finally, polyimide **IIIa** was obtained as a red powder after drying in an oven, under vacuum, at 100°C for 6 h.

Preparation of polymer films

Films of polymers **III** were prepared by casting a polymer solution of 8% concentration in NMP + 5% LiCl onto glass plates, followed by gradual heating from room temperature up to 210°C, and kept at 210°C for 1h. Dark-red, opaque coatings resulted having strong adhesion to the glass support. The resulting films were stripped off the plates by immersion in boiling water. They were kept in boiling water for further 2 h, followed by drying in oven at 110°C. These films had the thickness in the range of 40-50 µm and were used afterwards for various measurements.

Very diluted polymer solutions in NMP with concentration of 1% were used to obtain very thin films having the thickness in the range of nanometers onto silicon wafers by spin-coating technique, at a speed of 5000 rpm. These films, as-deposited, were gradually heated up to 210°C in the same way as described earlier to remove the solvent and then they were thoroughly washed with boiling water, and after drying they were used for atom force microscopy (AFM) investigations.

Measurements

The infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using KBr pellets or thin films having the thickness of 30-80 µm.

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

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) using a MOM Budapest derivatograph, operating at a heating rate of 12°C/min, in air, from room temperature to 750°C. The temperature of 5% weight loss on the TG curve was considered to be the beginning of decomposition or 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 precipitated polymers was determined by using a Pyris Diamond DSC Perkin Elmer calorimeter. 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 values of the polymers.

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

The morphology of the free-standing films was investigated by scanning electron microscopy (SEM) using a Quanta 200 ESEM.

The UV-Vis absorption and photoluminescence (PL) spectra of the polymers were registered with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, by using very diluted polymer solutions (approx. 10^{-5} M).

CONCLUSIONS

New heterocyclic polymers containing perylenediimide, oxadiazole and hexafluoroisopro-

pylidene groups in the repeating units were prepared by polycondensation reaction at high temperatures of an aromatic diamine containing oxadiazole ring, with a mixture 1:2 of perylenetetracarboxylic dianhydride and hexafluoroisopropylidene dianhydride. The imidization process was monitored by FTIR spectroscopy. These fluorinated polyperyleneimides containing oxadiazole rings are soluble in NMP and can be processed into tough and flexible free-standing films by casting technique. Very thin coatings with the thickness in the nanometre range were deposited by spin-coating technique on silicon wafers and they showed a high quality, without cracks or pinholes. SEM studies evidenced self-organized segregated structures of such films. The present polymers are highly thermostable, with decomposition temperatures above 470°C and glass transition temperatures in the range 220-290°C. By excitation with light of different wavelengths, the polymer which did not have ether bridges in the main chain exhibited two strong emission maxima in the bluish and green-yellow domains, due to oxadiazole and perylenediimide chromophore, respectively. At the same time, in PL spectra, those polymers which had some ether linkages in the main chain exhibited only the emission characteristic to perylenediimide chromophore and conjugated parts with imide rings, without emission from oxadiazole chromophore which was quenched due to the transfer of excitation energy from oxadiazole to perylene moieties. In solid state, these polymers did not show any photoluminescence. All these properties make the present polymers potential candidates for use in the manufacture of light-emitting devices having high stability.

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