

## High Performance Perylenediimide-Based Copolymers and Thin Films Made Therefrom

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The paper describes the synthesis and characterization of three copolymers containing perylenediimide units and other chromophores in the main chain, as well as various flexible groups as siloxane, hexafluoroisopropylidene or ether, with emphasis on their thermal and photo-optical properties. Very thin copolymer films were obtained from these polymers with smooth and homogeneous surfaces that are self-organized into vertically segregated structures. Upon irradiation with light of different wavelengths the polymers in solution showed photoluminescence maxima in the UV, blue or green-yellow spectral range. In solid state only a weak emission in the UV domain occurred due to aggregation of perylenediimide chromophores which leads to fluorescence quenching. The FRET phenomenon between oxadiazole to perylenediimide chromophores was observed to occur for which the oxygen bridge appear to be responsible.

**Keywords:** Poly(peryleneimide)s, Oxadiazole, Thin films, Optical properties, Photoluminescence.

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### 1. INTRODUCTION

Polymeric materials are distinguished by low density, flexibility, versatile electronic properties, chemical inertness and low cost. As a result, they have been extensively used in fields ranging from aerospace to microelectronics, optoelectronics, composites and fiber optics. The growth of modern technology has posed a constantly increasing need for materials that can perform well under harsh conditions, such as elevated temperatures. Polyimides have various outstanding characteristics such as good adhesion to metal, high thermal stability, low thermal expansion, excellent film-forming properties, and especially a high T<sub>g</sub>, of above 200 °C, which make them potentially useful as stable materials for electronic applications [1-3].

Among the polyimides, those containing perylene units appear to possess one of the highest thermal stability because of the condensed aromatic perylene ring. Perylene derivatives, with their promising electroactive and photoactive properties, have attracted a special interest for potential applications in organic molecular electronics. Perylene bisimides combine a strong absorption in the visible region with a fluorescence quantum yields near unity and a high stability towards photooxidation. Furthermore, perylene bisimides feature a relatively low reduction potential, which enables their use as an n-type semiconductor and as an electron acceptor in photoinduced charge transfer reactions. Because of their appealing properties, perylene monoimide and perylene bisimide derivatives have been utilized in various electronic and optical applications such as field-effect transistors, fluorescent solar collectors, electrophotographic devices, dye lasers, photovoltaic cells, and light-emitting diodes [4-8].

However, research using polyimides containing perylene in optoelectronic fields can rarely be found so far which may be due to the poor solubility of perylene-

diimide polymers in common organic solvents. Therefore, the design and preparation of soluble poly(peryleneimide)s, to give satisfactory processability of products without a perceptible loss of favorable properties, is an important and urgent problem in the chemistry of high performance polymers.

Here we report a study on the synthesis and properties of new processable copolymers containing perylene, oxadiazole and various flexible or voluminous units in the main chain. Such polymers are expected to have a useful balance of material properties and processing capability, particularly for casting into very thin films for various applications in optoelectronics. The properties of these copolyimides such as solubility, thermal stability, glass transition temperature, photo-optical as well as the morphology and quality of nanometric films made therefrom were investigated.

### 2. METHODS

#### 2.1 Monomers

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and hexafluoroisopropylidene-dianhydride (6FDA) have been purchased from Aldrich and used as received.

2,5-bis[4-(*p*-aminophenoxy)phenylene]-1,3,4-oxadiazole, 1,3-bis(4-phthalic anhydride) tetramethyldisiloxane and 1,3-bis(4-phthalic anhydride)-9,9-bis(*p*-hydroxyphenyl)fluorene were prepared following published procedures [9-11].

#### 2.2 Polymers

Copolyimides **PF**, **PSi** and **PFI** have been prepared by one-step polycondensation reaction of the diamino-oxadiazole with a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride and hexafluoroisopropylidene-, tetramethyl disiloxane- or fluorene-containing

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dianhydride, in N-methylpyrrolidinone (NMP) and lithium chloride (LiCl) as solvent, at a concentration of 7 % total solids, under nitrogen stream, at high temperatures. The monomer ratio was adjusted up to soluble and film-forming polymers were obtained.

In case of the two dianhydrides with different reactivity, the less active dianhydride monomer PTCDA was added in the first stage of reaction to the solution of diamine in NMP, and then the more active dianhydride monomer 6FDA, tetramethyl disiloxane- or fluorene-containing dianhydride was added to achieve a more even random incorporation of the two monomer units in the polymer chain. Owing to the low solubility of PTCDA in NMP + LiCl at room temperature, higher reaction temperature is necessary to make better solubility. The mixture was heated to 180–200°C under nitrogen for 6 h and then cooled to room temperature. The resulting dark red solution was poured into water, washed with plenty of water and finally treated with ethanol in a Soxhlet apparatus for 1 day in order to get rid of the unreacted monomers and high boiling solvent, followed by drying in an oven, under vacuum, at 100°C. The structure of copolyimides **PF**, **PSi** and **PF1** are shown in Fig. 1.

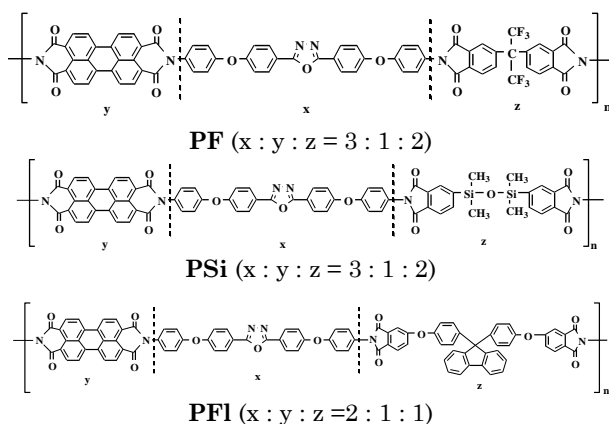


Fig. 1 – Structure of copolyimides **PF**, **PSi** and **PF1**

### 2.3 Preparation of polymer films

Very diluted polymer solutions in NMP with concentration of 0.5–1 % were used to obtain very thin films having the thickness in the range of nanometers onto silicon wafers, glass or quartz supports by drop-casting technique. These films, as deposited, were gradually heated from room temperature up to 200 °C to remove the residual solvent and were used for atomic force microscopy (AFM) and photo-optical behaviour investigations.

### 2.4 Measurements

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

The quality of very thin films as-deposited on silicon wafers was investigated by atomic force microscopy (AFM) using a Scanning Probe Microscopy Solver PROM, 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 STA 449 F1 Jupiter device (Netzsch, Germany) operating at a heating rate of 10 °K/min, in nitrogen, from 30°C to 900°C. The onset 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 DSC 200 F3 Maia (Netzsch, Germany) equipment. Approximately 4 to 6 mg of each polymer were crimped in aluminium pans and run in nitrogen atmosphere with a heat-cool-heat profile from 30°C to 200–250°C at 10°K/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 UV-Vis absorption and photoluminescence spectra of polyimides were registered with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, by using very diluted polymer solutions (approx. 10–5 M) and very thin films.

## 3. RESULTS AND DISCUSSIONS

New oxadiazole-containing copolyperyleneimides, **PF**, **PSi** and **PF1** containing various rigidity disturbing units as hexafluoroisopropylidene, siloxane or ether have been successfully prepared.

The structures of the present polymers were identified by infrared spectra. In the IR spectra of all the polyimides characteristic imide ring absorption bands appeared at 1770–1780  $\text{cm}^{-1}$  (asymmetrical C=O imide stretching), 1720–1730  $\text{cm}^{-1}$  (symmetrical C=O imide stretching) and 720–730  $\text{cm}^{-1}$  (imide ring deformation). Characteristic absorption peaks of 1,3,4-oxadiazole ring appeared at 960–970  $\text{cm}^{-1}$  and 1012–1020  $\text{cm}^{-1}$  (=C–O–C= stretching). C–H linkage in aromatic rings showed absorption peak at 3100–3120  $\text{cm}^{-1}$  while the C–F linkage showed absorption peak in the range 1100–1300  $\text{cm}^{-1}$ . The incorporation of tetramethyl disiloxane units in the polymer chain was evidenced by the clear absorption peaks in the range of 2960–2950  $\text{cm}^{-1}$  (aliphatic C–H stretching, CH<sub>3</sub> groups), 1250–1240  $\text{cm}^{-1}$  (Si–CH<sub>3</sub> deformation), 1120–1110  $\text{cm}^{-1}$  (silicon–phenyl bond), 1070–1060  $\text{cm}^{-1}$  (Si–O–Si asymmetric stretching) and 800–790  $\text{cm}^{-1}$  (Si–CH<sub>3</sub> stretching). Strong absorption bands in the range of 1250–1240  $\text{cm}^{-1}$  in the FTIR spectra of copolyimides were assigned to the aromatic ether stretching.

It is known that conventional aromatic poly(peryleneimide)s are insoluble in easily 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 inter-chain interactions and due to the compact aggregation of the polymer chains which occurs during imidization that is carried out at high temperatures. Our copoly(peryleneimide)s are soluble in a convenient aprotic amidic solvent which is NMP, at a concentration of

0.5 – 1% due to the presence of the flexible 6F or siloxane groups, or of voluminous fluorene units in the main chains.

All these copolyimides are highly thermostable, as evaluated by thermogravimetric analysis, their initial decomposition temperature being above 475°C (Table 1). The temperature of 10% weight loss ranges from 482°C to 505°C. The temperature of maximum rate of decomposition was found in the domain of 520°C – 557°C. These data demonstrate that all the polyimides have high thermal stability, which is not affected by the introduction of the flexible 6F, siloxane or other units in the main chain, while the solubility, hence the processability of the resulting copolymers are much improved due to the presence of these groups. Representative TG and DTG curves of these polymers are shown in Fig. 1.

**Table 1** - Thermal properties of the polymers

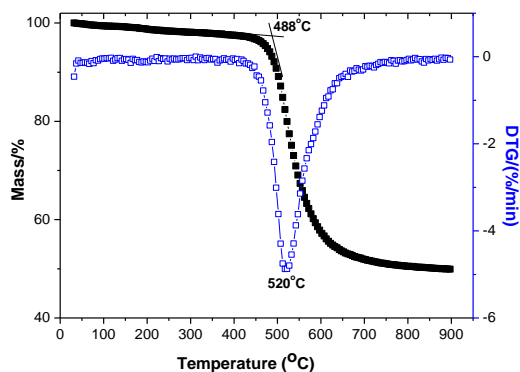
Polymer	T <sub>g</sub> (°C)	IDT(°C)	T <sub>10%</sub> (°C)	T <sub>max</sub> (°C)
PF	267	475	482	530
PSi	187	488	501	520
PFI	304	483	505	557

T<sub>g</sub> – glass transition temperature

IDT – temperature of 5% weight loss

T<sub>10%</sub> – temperature of 10% weight loss

T<sub>max</sub> – temperature of maximum rate of decomposition

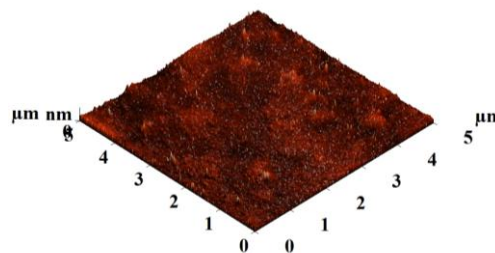


**Fig. 1** – TG and DTG curves of PSi

The glass transition temperature of the polyimides was evaluated by differential scanning calorimetry (DSC). All these polymers exhibit glass transition in the range of 187 – 304°C (Table 1). It can be seen that there is a large influence of the structure of the five-member dianhydride on the glass transition temperature, the lowest being obtained in the case of tetramethylsiloxane-containing dianhydride and the highest in the case of fluorene-containing dianhydride.

Very thin films having the thickness in the nanometer range were deposited by drop-casting technique onto silicon plates, by using diluted solutions of polymers (concentration of 1%). The morphology of these films as-deposited onto silicon plates was studied by atomic force microscopy (AFM). The copolymer films are smooth and homogeneous and are self-organized into vertically segregated structures. The root mean square roughness (RMS) is in the range of 2 – 5 nm

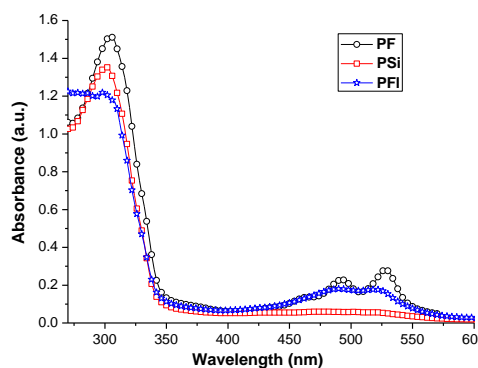
over a scanning area of 5 × 5 μm. A typical AFM image is shown in Fig. 2.



**Fig. 2** – AFM images of copolyimide PF (top: 2D image, down: 3D image)

Since 1,3,4-oxadiazole ring and perylene-diimide unit are known as light-emissive [8,12], the light-emitting properties of these polymers incorporating both perylene-diimide and oxadiazole fluorophores were investigated. The light-emitting ability was assessed on the basis of the UV-Vis and photoluminescence spectra which were recorded for both polymer solutions in NMP and polymer films cast from NMP solutions, after excitation with light of different wavelengths.

Those copolymers in solutions show one strong UV absorption maximum in the range of 302 – 307 nm due to diphenyl-1,3,4-oxadiazole chromophore, and in the case of PFI there are three additional small peaks like fingers at 275, 286 and 298 nm specific to fluorene unit (Fig. 3).



**Fig. 3** – UV-Vis absorption spectra of copolymers in solution

Three peaks at 452 – 462, 488 – 492 and 521 – 528 nm due to the absorption of perylene-diimide chromophore appeared only in the UV spectra of PF and PFI, and no significant absorption was registered for PSi. However, for polymers PF and PFI, these absorptions determined by the chain segments containing perylene-diimide units are much lower in intensity as compared with the absorption bands characteristic of diphenyl-1,3,4-oxadiazole or fluorene units.

In thin films, both polymers displayed one large absorption maximum centred in the range of 296 – 317 nm assigned to π-π\* transitions involving oxadiazole chromophore, being slightly blue- or red-shifted with respect to the absorption of the isolated molecules. Two additional weaker absorption peaks were detected as well at 495 – 503 and 530 – 543 nm, being responsible for the absorption of perylene-diimide only for PF and PFI. In the UV-vis spectrum the PSi very weak,

insignificant absorption peaks characteristic to perylenediimide unit were observed. Fig. 4 compares the UV spectra of the thin films made from **PSi** and **PFI**.

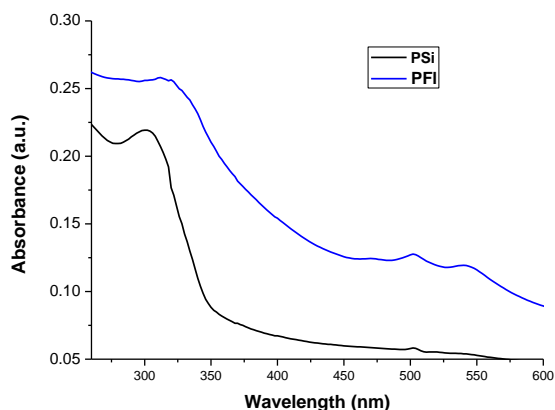


Fig. 4 – UV-Vis absorption spectra of **PSi** and **PFI** thin films

The fluorescence behaviour of these polymers was investigated by exciting with light of two different wavelengths, one characteristic to oxadiazole chromophore and another one characteristic to perylenediimide chromophore. When excited with UV light of about 300 nm, the polymer solutions showed one broad weak emission in the UV domain, in the range of 368 – 375 nm, and two PL emission peaks within 536 – 539 nm and 574 – 578 nm range, in the case of **PF** and **PFI**, which are due to perylenediimide. **PSi** showed only one strong emission peak at 524 nm, being characteristic to this chromophore. Since the absorption maximum of the diphenyl-oxadiazole chromophore is approx. 304 – 306 nm and the perylenediimide moieties did not directly absorb these wavelengths light, an excitation energy transfer (known as FRET phenomenon) from oxadiazole to perylenediimide occurred. Fig. 5 shows photoluminescence spectra of these polymers in solution by excitation with light peaking at about 300 nm. The emission spectra in NMP solution excited by a 492 nm light, showed two peaks at 534 – 537 nm and 575 – 578 nm, which corresponded to the emission of perylenediimide moieties.

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The photoluminescent behavior of these copolyimides changed significantly from solution to solid state. The light-emitting ability of these polymers was observed only by exciting at about 300 nm. The PL spectra present one emission maxima in the UV domain at 360 and 369 nm only for **PSi** and **PF**, respectively, and several shoulders in the blue domain at 418, 444 – 457, 482 – 487 nm and 523 nm, due to the emission of diphenyl-oxadiazole/fluorene, imide and phenylene segments for all polymers. When the excitation was done with UV light of 490 or 520 nm no emission attributed to perylenediimide chromophores that absorb this visible light was observed. This behavior can be ascribed to the high content of perylenediimide chromophore which leads to fluorescence quenching through aggregation.

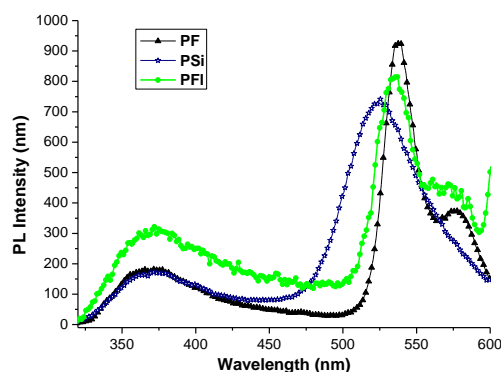


Fig. 5 – Fluorescence spectra of perylenediimide-based copolymers by excitation with UV light peaking at about 300 nm

## 4. CONCLUSIONS

The high-performance properties of these copolymers provide an important guideline for the design of new materials that can be used to fabricate electro-optical devices with high stability.

## ACKNOWLEDGEMENTS

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