Annex no. 4

ROMANIAN ACADEMY
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HABILITATION THESIS

TITLE: *Macromolecular architectures containing 1,3,4-oxadiazole or/and imide rings for high performance materials*

Fundamental domain: **CHEMISTRY**

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A B S T R A C T

The habilitation thesis entitled "**Macromolecular architectures containing 1,3,4-oxadiazole or/and imide rings for high performance materials"** highlights the results of the research activity carried out by its author after defending the PhD thesis (June 2005) and comprises three main parts.

Part I (Scientific achievements) is the pillar of this thesis, reflecting the scientific interest in the field of "*High performance aromatic and heteroaromatic polymers for advanced technologies (electronics, optoelectronics, biomedicine, environmental protection and alternative energies)*". **The original contribution** consists of the discovery of **innovative materials** by developing new concepts and high-tech scientific methods to evidence the particular properties of investigated macromolecular architectures that recommend their use in high performance applications, in agreement with the stringent demands of the modern technologies. The basic concept of the author contributions is the design, synthesis and rigorous characterization of new macromolecular compounds based on various thermally stable heterocycles having electric charge transporting or dielectric properties, light-emitting ability or high optical transparency, electroactivity or liquid crystalline behavior. The present thesis provides an overview of the main scientific achievements organized in three thematic directions.

a) *Polymer architectures containing 1,3,4-oxadiazole rings and various functional groups for advanced materials*

Two series of poly(oxadiazole-amide)s were synthesized with the aim to develop processable high-performance polymers with potential applications as photo- and electroluminescent materials or gas separation membranes. The investigated polymers are highly thermostable, and some of them are semicrystalline and form plastic mesophases. They exhibit blue photoluminescence, very good electron injection properties and can be processed into transparent, defectless and hydrophobic free-standing films having low dielectric constants. The membranes obtained from these polymers exhibit good gas permeation properties and maintain them at high temperature.

Another trend of this chapter was the preparation of new copolymers of maleic acid with styrene or *N*-vinylpyrrolidone functionalized with oxadiazole units and the study of their fluorescence in correlation with the morphology and crystallinity. Excited with UV light of different wavelengths, these semicrystalline copolymers showed UV- and/or blue-light emission. The very thin films prepared therefrom were homogeneous, two of them exhibiting microporous or spherulite-like morphology. Two of these copolymers derived from *N*-vinylpyrrolidone were tested on osteosarcoma cells, showing a cytotoxic effect of up to 56%. In addition, the biomimetic synthesis of $CaCO_3$ particles from aqueous solutions in the presence of one of these polymer conjugates as template and their adsorption capacity was thoroughly investigated.

b) Advances in imide-type polymer architectures

Two series of highly fluorinated polyimides were prepared that, besides high thermal stability, over 490°C, displayed high optical transparency and blue- or green-yellow light emission ability depending on the chromophore nature. The highly hydrophobic thin films prepared from such polymers presented neat, vertically segregated or porous morphology.

Another direction of study was achievement and characterization of new fluorinated polyimide blends. Various characterization techniques have been involved to demonstrate the homogeneous mixtures at the molecular level, both intramolecular and intermolecular charge transfer interactions in solid state contributing to the good miscibility. Various morphologies were found for these new blend films: some were amorphous with spherical entities dispersed on the surfaces, whereas the others displayed vertically segregated structures, with interlamellar or interfibrillar segregation. All polyimide blends showed high thermal stability, good mechanical properties, high transparency in the visual light range, low dielectric constant values and good gas

transport properties. Such polyimide blends can be exploited in applications such as gas separation membranes, interlayer dielectrics or transparent flexible substrates.

On the other hand, new structurally designed poly(imide-amide)s were synthesized in which naphthylimide and amide units are directly connected through a N-N bond, having unexpected, multifunctional properties. They form nanometric aggregates in solutions and can be processed in thin films having self-assembled micellar structures. These films exhibit good electron injection and transport properties, and can be electrochemically doped. In addition, such polymers display good thermal stability, up to 370^{o}C, and potential for white- and blue-light emission in solutions and films, respectively.

c) Polymer architectures containing imide and 1,3,4-oxadiazole heterocycles for high-tech applications

New polyimides containing 1,3,4-oxadiazole rings, specially designed for use as high performance materials in electronics and optoelectronics, have been synthesized. These polymers were easily soluble in polar amidic solvents, allowing their processing into thin flexible films with good mechanical strength. The main absorption maximum of oxadiazole-containing polyimides is centred at 300 nm, while their photoluminescence upon irradiation with UV light occurred in the blue spectral range. X-ray measurements indicate a semicrystalline state of the oxadiazole-containing polyperyleneimides, which consists in columns of perylene units arranged face-to-face, with different orientations and statistically distributed into amorphous matrix of the polymer. Polyimides containing oxadiazole rings displayed low dielectric constant values, even lower than that of the conventional polyimide Kapton. Some free-standing films showed high optical transparency, with an average transmittance in visible region of 76%, being promising for optical applications. The presence of 1,3,4-oxadiazole rings in the polyimide structures afforded very good electron injection and transport properties. The static ablation of poly(oxadiazole-imide) films with excimer laser operating at 248 nm (KrF) produced a carbon substrate on the top of the surface that acts as a barrier for laser radiation, protecting the polyimide material. Thus, superhydrophobic surfaces were obtained that may find applications as self-cleaning materials. Some polymer films displayed the ability to orient liquid crystals on patterned surfaces.

Part II (Perspectives, future research directions, career evolution and development plans) briefly highlights the main professional and academic achievements as PostDoc researcher. Thus, my scientific activity after the Ph.D defense is reflected in the high number of publications achieved in the field of thermostable heterocyclic polymers and materials based on them for high-performance applications, as follows: 64 peer-referred articles (most ISI), 2 book and 2 book chapters, 29 papers in conference proceedings and 61 oral presentations (conferences or lectures), coordination of 3 research projects and participation as team member in other 14 projects. Presently my Hirsch index is 16 (cumulative Damaceanu MD or Iosip MD) and own papers have been cited in 448 prestigious ISI articles (without self-citations). I have been awarded "Nicolae Teclu" Award of the Romanian Academy (2012) and the National Science and Art Foundation Award (2013).

The career evolution and development plan are based on five generic objectives and outlines the research topics that will be continued or will be developed in the next years, particularly targeting the applied branch of heterocyclic and heterochain polymers. This part presents the main strategies, indicators to quantify the professional and academic activities, as well as the future work in order to accomplish the proposed objectives. One of them foresees to attract Master and PhD students in research activities related to high performance polymers.

It must be emphasized that maintaining and creating lasting relationships with future members of my team, with external entities such as companies, and members of the academic community, promoting the ideas of scientific progress and transparency, developing a modern and competitive field are the main directions on which I will insist in the next period.

The habilitation thesis ends with ***Part III (References)*** that lists the main bibliographic data related to the matter of the first two parts.