ROMANIAN ACADEMY
SCOSAAR

"Petru Poni" Institute of Macromolecular Chemistry

HABILITATION THESIS

TITLE: FUNCTIONAL POLYMERS WITH PHOSPHORUS- AND/OR NITROGEN-CONTAINING RINGS FOR ADVANCED APPLICATIONS

-Abstract-

Fundamental domain: CHEMISTRY

Habilitation domain: CHEMISTRY

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Thesis presented to obtain habilitation certificate in order to coordinate doctoral activities in the CHEMISTRY domain

IAŞI, 2016

- A b s t r a c t -

The habilitation thesis presents some original and relevant research results, obtained after I defended the doctoral thesis (1996), in the field of heterocyclic polymers with special properties for high performance applications, especially those concerning development and evaluation of new multifunctional polymeric systems containing cycles with phosphorus and/or nitrogen atoms.

The thesis is divided in three sections. The first section contains three chapters including some of the original contributions to the development of polymers with fire resistance properties, significant results achieved in the field of polymers containing cycles with nitrogen atoms, such as imide, 1,3,4-oxadiazole, phenylquinoxaline, as well as new research results in the field of polyimide nanocomposite films based on inorganic compounds like silica, zeolites, titanium dioxide nanotubes and carbon nanotubes.

The first chapter outlines the best results achieved in the field of polymers with fire resistance properties, focusing on the compounds whose structures contain cycles with phosphorus atoms. Starting from 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), different phosphorus-containing monomers were synthesized and used to prepare various polymers showing improved properties: aromatic polyesters having DOPO side groups, polyphosphates and polyphosphonates containing phosphorus both in the side and main chains, aromatic polyesters having liquid crystal properties, polyesterimides with DOPO groups and polydimethylsiloxane segments. The physical properties of the resulting polymers, such as solubility, liquid crystal behaviour, thermal stability, limiting oxygen index, were investigated by different techniques and discussed in correlation with their structure. Structure-properties relationships useful designing new compounds with tailored properties were established. A comparative kinetic study of the thermal degradation reactions of some polyesters and polyesterimides with and without phosphorous was also performed using different methods: Coats-Redfern, Kissinger and Vyazovkin. The fire resistance of epoxy resins was improved by using two methods: the incorporation of DOPO groups and polydimethylsiloxane segments into the cross-linked structure or the use of a polyphosphoester as a flame retardant having high-efficiency and good compatibility with the epoxy resin. The study concerning fire resistance properties was performed in the frame on an International STREAM Project in cooperation with the AIDICO Institute from Novelda-Alicante, Spain. By using a small percentage of oligophosphonate (equivalent to 1% phosphorous), a very good fire resistance of the cross-linked epoxy resin was obtained. The research results in the field of phosphorus-containing polymers with flame resistance properties and/or liquid crystalline behaviour were published in prestigious journals such as Journal of Materials Chemistry A, Journal of Polymer Science Part A: Polymer Chemistry, Polymer, European Polymer Journal.

The second chapter deals with original aspects related to the polymers with nitrogen-containing rings. Aromatic polyethers containing 1,3,4-oxdiazole or phenylquinoxaline rings were obtained and studied. The thermal, electrical and optical characteristics were evaluated in connection with their structure. The influence of solvents and solvent mixtures on the optical properties of some prepared polymers was analyzed, the chromaticity diagrams were built and the quantum yield was determined. Thermal decomposition was investigated by TG/MS/FTIR technique and a mechanism of the thermal degradation in air as well as in inert medium of helium was proposed. Polyamides and polyamidimides with side groups having 1,3,4-oxadiazol ring were also prepared based on new diamines, such as 2-(4-dimethylaminophenyl)-1,3,4-oxadiazole, or 4,4′-diamino-4″-[2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole]triphenylmethane. The optical properties both in solution and in film were investigated. Solutions of the polymers exhibited fluorescence in the blue region having high values of quantum yield. The reduction in fluorescence was studied in the presence of 2,5-dinitrophenol using the Stern Volmer equation.

One of the most interesting research refers to a polymer containing 4-imidazolidin-2-one rings which was obtained starting from a cyclic monomer 1,3-diacetyl-imidazolin-2-one, through a special melt polymerization process. It was used further in the synthesis of poly(methylene amine), a new polymer having the highest concentration of amine groups on the structural unit, being for the first time reported in the literature. Poly(methylene amine) marks a limit to the degree of functionalization and, in its protonated form, exhibits high charge density. Additionally, this polymer can lead to a wide variety of new polymers due to the reactions of amine groups, such as alkylation, acylation and cyclization. This work was performed in the frame of a research stage at the Max-Planck Institute for Polymer Research from Mainz-Germany. The results were published in a journal with high impact factor that proves the importance of this research: Angewandte Chemie International Edition.

The third chapter presents some results on the preparation and study of some polyimide composite films based on different inorganic compounds. It was followed to obtain materials with improved characteristics as regards its mechanical, thermal, gas separation and nanoactuation properties. Silica-containing polymer films having a uniform distribution of the silica particles and better compatibility between the inorganic and organic phases were prepared by sol-gel technique. The influence of the silica content and of the chemical structure of the polyimide matrix on the thermal, mechanical, and electrical properties of nanocomposite was investigated. Polymer films containing zeolite nanoparticles were obtained by direct mixing technique in solution. The surface quality of the films, morphology and gas separation properties were studied. It has been observed that the gas permeability increased with increasing zeolite content while selectivity for O_2/N_2 and CO_2/N_2 was maintained at a high level. Polyimide nanocomposites containing TiO_2 nanotubes or a mixture of TiO_2 and carbon nanotubes were prepared. The thermal and electrical properties, as well as the effect of type and filler content on nanometric displacements when an electric voltage was applied on the film surface were determined in cooperation with INCDIE ICPE-CA, Bucharest.

The second section of habilitation thesis presents the evolution and independent development plan of the professional career. This relates to the continuation of themes of the projects that are in progress and addressing new directions of interest from the scientific and practical point of view. The main research directions that will be addressed in the future are briefly described and documented in the overall context of the significant scientific achievements in the field. They consist in: developing and discovering new biodegradable and biocompatible polymers for biomedical applications; novel fire resistant polymeric materials, mainly based on polymers with a high content of phosphorus, to provide maximum efficiency and minimum risk to the user; polymers and composites with high dielectric constant; multifunctional polymers with high performance properties: optical (photoluminescence), liquid crystal behavior, superior characteristics for gas separation membranes.

The last section of the thesis includes references list associated with the thesis content and presented in the order indicated for the first time in the text. The list includes 312 articles, 54 of them being own articles (22 as prim author).