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EXPLORATORY RESEARCH PROJECT

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**COMPLEX SYSTEMS BASED ON
POLYMERS CONTAINING ALICYCLIC STRUCTURES
FOR HIGH PERFORMANCE APPLICATIONS**

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BRIEF REPORT

concerning the results obtained by the project team between 16

December 2015 – 5 October 2016

Objective 1. Morphological modification of bulk copolyimides (CPIs) into micro- and nano- porous particles to obtain materials for high performance applications

Associated Activities:

1.2. Micro- and nano- structured copolyimides by reprecipitation method

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1.2. Micro- and nano- structured copolyimides by reprecipitation method

Polymeric micro- and nanoparticles (NPs) are of broad interest in many specific surface applications including advanced materials, drug delivery, medical imaging, etc. The control of size and shape is essential in the development of polymeric particles (PIPs) as tools and products for a variety of fields.¹

Obtaining of PIPs

Literature data show three main directions on getting the polyimide particles (PI Ps), namely:

- (1) PI Ps preparation starting from PAA solution or PAA particles based on the solubility difference between the PI and PAA dissolved in the same solvent - e.g., 1-methyl-2-pyrrolidone anhydrous (NMP), N,N'-dimethylacetamide (DMAc) - which act as good solvents for PAA and as poor solvents for PI;
- (2) PI Ps preparation starting from a PI solution, by the solution cooling or by the dropwise addition of a precipitant (water or ethanol) into the polymer solution - methods useful only for the soluble PIs (being known that PIs are usually insoluble in common solvents);
- (3) composite PI Ps fabrication from PIs and other materials (e.g. PS, silica) by the reprecipitation method.

The reprecipitation method is a convenient technique for fabricating organic and polymer nanoparticles and/or nanocrystals in a dispersion medium. This approach is considered by some authors as a "kind" of solvent displacement method which transfers the molecule from the "good" solvent to the "bad" solvent, on condition that the molecule should have a limited solubility.

During this stage new polymer particles based on a partial-alicyclic copolyimide (CPI) derived from bicyclo [2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) were obtained by reprecipitation method.

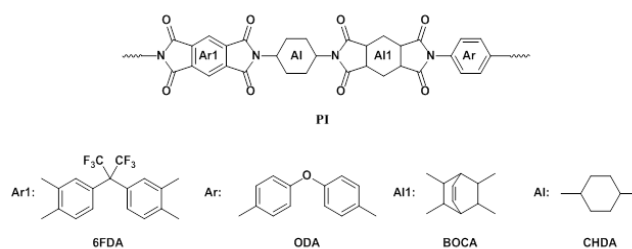
Both structural forms, the polymer precursor of polyimide - poly (amic acid), PAA- and the final polyimide form, PI, were used to prepare the polymeric particles. Their size ranged in size from nano to micro size due to differences in thermodynamic phase separation stabilizer systems used and efficiency, factors crucial role on the formation of particle morphology.

Table 1. Materials used in the PIPs syntheses

Chemical Name	Provider	Abbrev.	Purification method
Bicyclo[2.2.2]-7-octene-2,3,5,6-tetracarboxylic dianhydride	Aldrich	BOCA	Recrystallization from acetic anhydride, vacuum dried at 160°C, p.t. = 248°C
4,4'-(Hexafluoroisopropylidene)-diphthalic anhydride	Aldrich	6FDA	Recrystallization from acetic anhydride, vacuum dried at 160°C, p.t. = 244°C
4,4'-oxydianiline	Aldrich	ODA	Recrystallization from ethanol; p.t. = 189°C
trans-1,4-cyclohexan-diamine	Aldrich	CHDA	Recrystallization from n-hexane; p.t. = 70°C
N-methyl-2-pyrrolidone	Aldrich	NMP	Vacuum distillation at 10 mmHg, dried on CaH ₂ , stored on 4 Å molec. sieves
polyvinyl alcohol	Aldrich	PVA	Used without purification

Copolyimide synthesis

The CPI was synthesized by a two steps polycondensation reaction, from selected aliphatic/aromatic pairs of monomers, namely BOCA/ 6FDA as dianhydrides and CHDA/ ODA as diamines respectively (Scheme 1).



Scheme 1. The chemical structures of CPI and the selected monomers

Structural characterization. CPI: The copolymer has a number-average molecular weight, M_n , of 70 000 g/mol, is thermally stable above 300 °C and is well soluble in NMP, DMAc, N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), respectively at room temperature.

The polymer solubility is the result of a synergistic effect induced by the statistical nature of the macromolecular chains, and the chemical nature of the monomer sequences (coplanar and non-coplanar alicyclic, flexible connections, etc.), respectively, which, by cumulative effects reduce the chains symmetry, rigidity, interchain interactions and their packaging. Details of the synthesis and characterization: [J Polym Res, 21\(9\), 2014, DOI:10.1007/s10965-014-0514-4](#)

Using the copolyimide in both its structural forms, PAA and PI, polymeric particles with nano-(PINPs) and micro- (PIPs) sizes respectively were prepared.

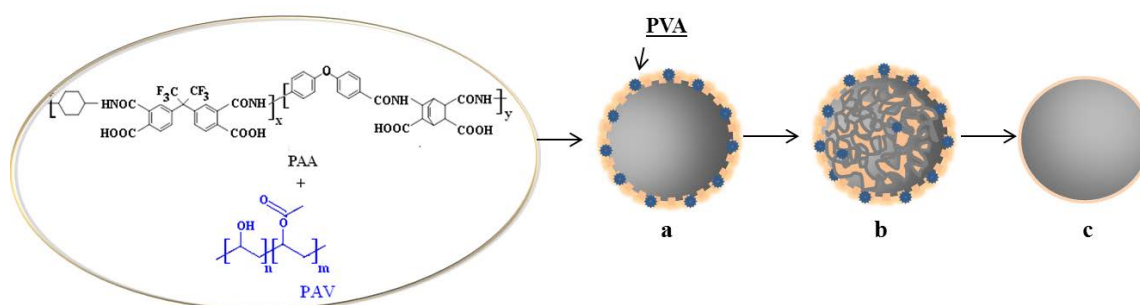
Their size ranged from nano- to micro dimensions due to the differences in the phase separation thermodynamics of the used systems and of the stabilizer efficiency, factors with fundamental role on the particles morphology formation.

PI NPs from PAA solution precipitation

PAA NPs were firstly prepared by the reprecipitation from the PAA solution.

The resulting **PAANPs** were converted to **PINPs** through chemical imidization in the dispersion medium, at room temperature, using as cyclodehydration agents acetic acid anhydride and pyridine. A mixture of two polar amide solvents, DMAc/ NMP was selected as *good solvent*, cyclohexane was chosen as *poor solvent*, while, polyvinyl alcohol (PVA) was used as *porogen*.

The initial droplets were obtained by injecting a DMAc/NMP solution containing PAA and PVA in cyclohexane (Scheme 2). Both PAA and PVA start to precipitate forming distinct micro phases, beginning with the surface layer of the droplets (Scheme 2 a, b).



Scheme 2. A possible representation of the PINPs formation

Some from the factors which influence the particles morphology (by the porogen molecule migration inside the droplet and the microphases separation, respectively) are:

- ✓ the porogen chemical structure,
- ✓ the solubility parameter (porogen/PAA compatibility),
- ✓ the porogen molecular weight and
- ✓ the mutual diffusion.

Taking into account:

- (i) the high hydrophobicity of the used copolyimide (due to its fluorinated and non-polar alicyclic units),
 - (ii) the pronounced hydrophilic character of PVA together with its high molecular weight and
 - (iii) the data from Table 1 showing that the cyclohexane is a much poorer solvent for PVA than for PAA,
- it becomes plausible the assumption of a PVA superficial layer formation outside, at the interface of droplets. For the both used PVA concentrations (25 wt% and 50 wt%) nonporous PI NPs were obtained (Scheme 2c).

Table 2. Solubility parameter of the compounds used in this study*

Compound	PAA	PVA	NMP	DMAc	cyclohexane
Solubility parameter (Mpa ^{1/2})	24.84	30.5	23.1	23.3	16.8

* Calculated by the Van Krevelen method

The obtained results are consistent with the literature data which mention as “suitable porogen” for such type of experiments a qualitatively compatible one with PAA by comparing the solubility parameters.

Spherical nonporous nanoparticles, with unchanged morphology before and after imidization resulted, in according with the literature data. The obtained morphology is explainable taking into account the fundamental role of the solubility parameter in a microstructure formation and considering the big difference between the solubility parameter of PAA and PVA used in our experiment (Table 1). The porogen molecular weight plays also an important role.

The morphology of the obtained structures was analyzed using transmission electron microscopy (TEM). TEM images (Figure 1) reveal particles with spherical shape and diameters in the range of 10÷700 nm.

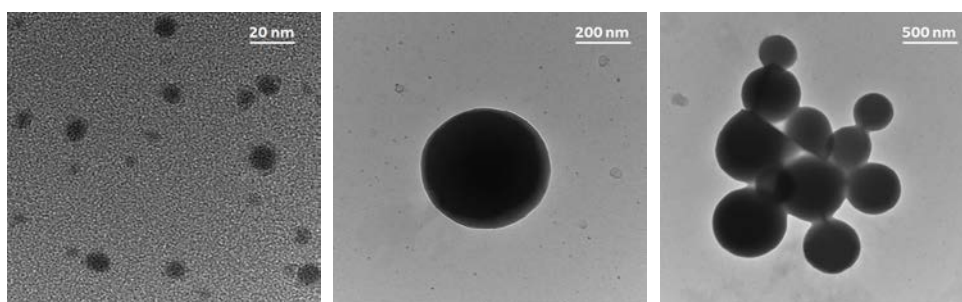


Figure 1. TEM images for PI NPs prepared from DMAc /NMP solution of PAA with PVA (50 wt %)

The TGA measurements data, displayed in Figure 2, demonstrate that the thermal behavior of the chemically imidized PINPs (PVA 50 wt %) - Figure 2b - is comparable to the ordinary PINPs, with 5% weight-loss at about 275°C - Figure 2 a.

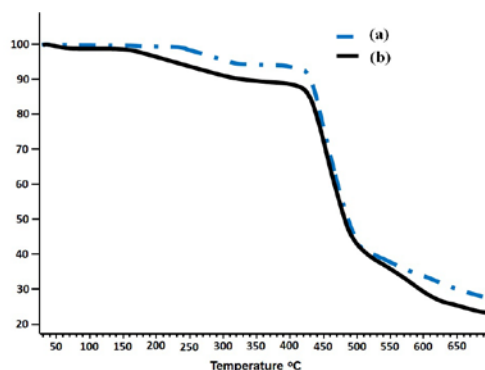


Figure 2. TGA (weight loss) curves for: (a) PI and (b) chemically imidized PI NPs (PVA 50 wt %)

The result suggests that there is no amount of PVA inside of the particles. A similar conclusion can be detached from the FTIR analysis (Figure 3).

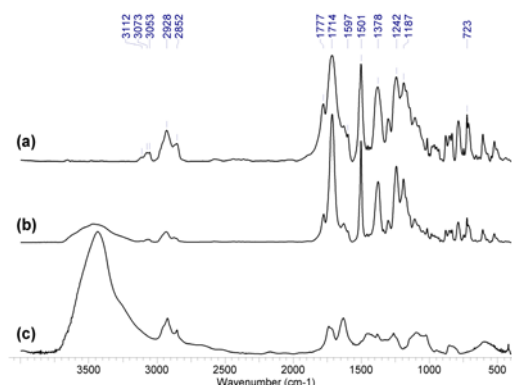


Figure 3. FTIR spectra for: (a) PI, (b) chemically imidized PI NPs (PVA 50 wt %) and (c) PVA

The FTIR spectra confirmed the imide structure by similar signals at 1777 and 1714 cm^{-1} (C=O imide symmetric and asymmetric stretching vibration) and at 1378 cm^{-1} (C-N imide ring stretching vibration) in the both ordinary and chemically imidized PINPs structures. *This finding supports the thermal behavior data.* Other similar signals are: 723 cm^{-1} (imide ring deformation vibration), 711 cm^{-1} (C=C bond from the bicyclic structure²², 1242 cm^{-1} (ether bridge), 1378 cm^{-1} (hexafluoroisopropylidene groups).

PI Ps from PI solution precipitation

PI Ps were obtained by a combined method consisting of the dropwise addition of a precipitant in a PI solution and sonication, adopted in order to achieve the liquid–liquid phase separation. A polymeric stabilizer, PVA, was used.

The particle size and particle size distribution are decisively impacted by:

- ✓ the initial drop size distribution of the polymer/water dispersion,
- ✓ the breakage/coalescence process
- ✓ and the non-equal absorption of the polymer into droplets, respectively.

The drop size uniformity will increase by decreasing the aggregation phenomenon and the coagulation.

In this respect we used two methods:

- the adding of the precipitant solution into the polymer solution to obtain the “liquid–liquid demixing” effect and
- the using of PVA as polymeric stabilizer, able to act as protection against the collision and aggregation of the droplets.

Table 3. Polyimide particles preparation

Sample code	PI concentration (g/mL)	PVA concentration (g/mL)	T (°C)	Sonication time (')
PIPs (a)	0.02	0.02	80	120
PIPs (b)	0.004	0.02	80	120
PIPs (c)	0.004	0.04	80	120

The precipitant was added and after the beginning of the phases separation To ensure a continuous and complete precipitation in system. A larger precipitant quantity provides better droplets isolation and facilitates the solvent removal. The particles shape and size are dependent on the system conditions, especially on the polymer and stabilizer concentration.

Table 3 presents the experimental conditions for the particles preparation while Figure 4 shows morphological aspects of the microparticles surface investigated by atomic force microscopy (AFM).

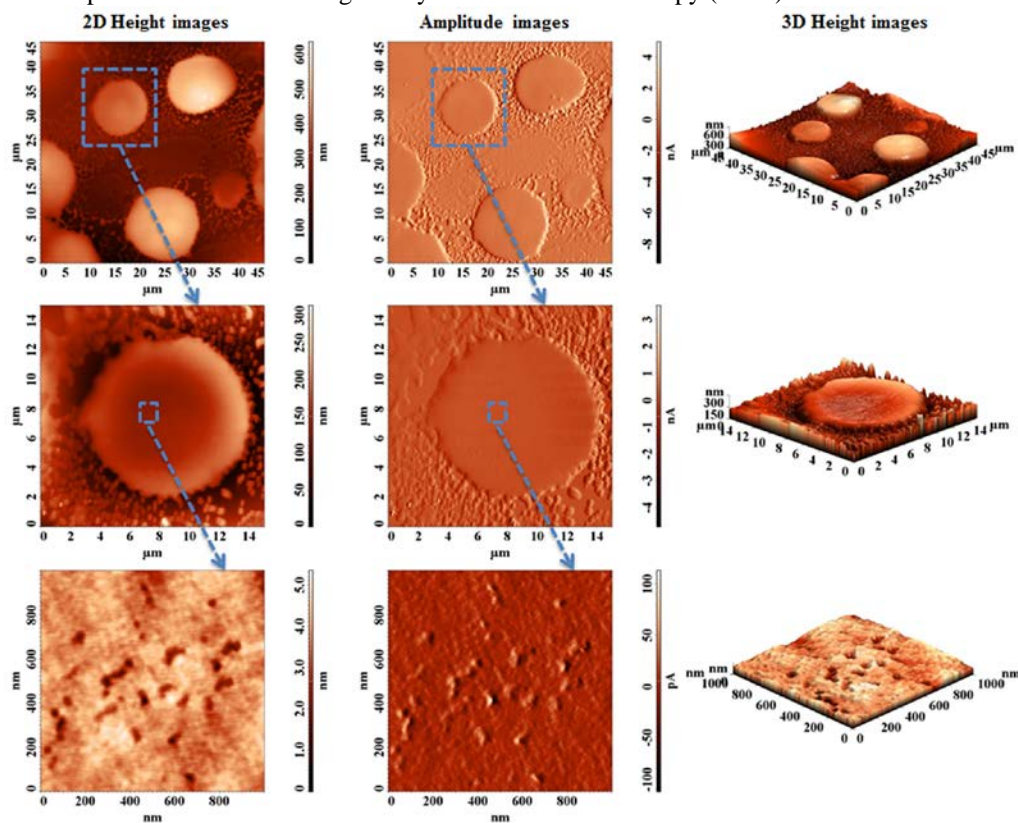


Figure 4. Height and corresponding amplitude AFM images of the microparticles surface on different scan sizes for the PI Ps (a) sample

Height and corresponding amplitude images highlighted the existence of microparticles with a relative spherical shape (sometimes ellipse or formless) and an average diameter of $12.28 \pm 1.75 \mu\text{m}$. Each microparticle membrane presents nanopores with an average diameter of $34 \pm 8 \text{ nm}$, randomly distributed all over the surface.

As it can be seen some pores are individual and well defined and others tend to approach each other. Analyzing the individual ones and calculating the average value of the shape factor, namely $f_{shape} = 1.21 \pm 0.35$, using the pore area A and perimeter, P ($f_{shape} = 4\pi A / 1.064 P^2$)¹⁸ on can conclude that the porous formations have a smooth circumference.

Regarding the elongation level of the pores, the elongation factor was also evaluated using the minimum d_{min} and maximum Feret diameter d_{max} ($f_{elong} = d_{min} / d_{max}$)²⁴. The average elongation factor close to 1 ($f_{elong} = 0.89 \pm 0.11$) describes an almost circular contour of the pores.

All the mediations were performed on 10 arbitrary selected particles.

Analyzing the influence of the polymer concentration on the particles morphology, SEM results reveal that, when the polymer concentration decreases from 0.02 to 0.004 g/mL (Table 2), the particles shape change from elliptical (sometimes) – Figure 5a – to spherical one – Figure 5b,c – while the their size decreases. For the lowest polyimide concentration, microspheres with sizes between $1.2 \div 3.7 \mu\text{m}$ were obtained. Figure 5 presents some illustrative scanning electron microscopy (SEM) images of the resulting PI particles.

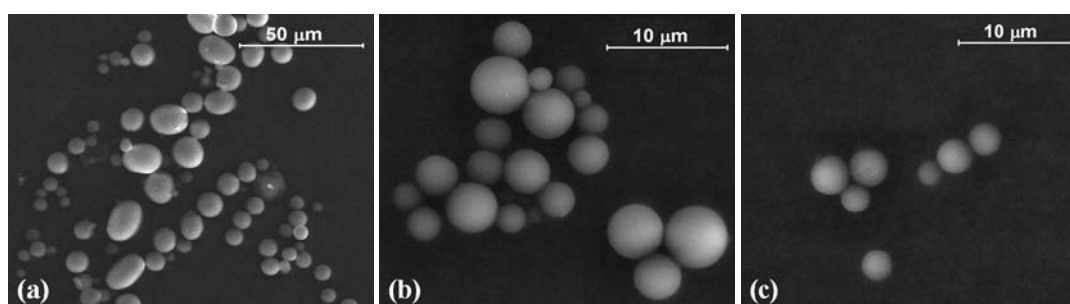


Figure 5. SEM images for the samples: PI Ps (a), PI Ps (b) and PI Ps (c)

The laser light scattering (LLS) data allow us to observe that the systems polydispersity decreases (by increasing the PVA solution concentration) from 0.214 for the system PI Ps(b) to 0.132 for the system PI Ps(c), while microspheres size remains almost constant, in the range of $3030 \div 2770 \text{ nm}$ (Figure 6).

This could be associated with the fact that the stabilizer concentration practically does not influence the number of the primary droplets formed in solution. The relatively large size and narrow size distribution may be considered to be the mechanism result of the particle formation when, during the precipitation process, any droplet can alike absorb polymer from solution.

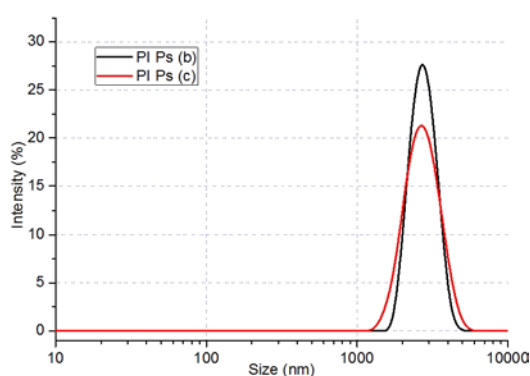


Figure 6. Particle size distribution for the systems noted PI Ps(b) and PI Ps(c) from Table 3

From the point of view of the thermal stability, the results showed that the obtained PI Ps present a 5% weight-loss at 285°C , comparatively with the ordinary PI which has 5% weight-loss temperature at 310°C .

Conclusions

- ✓ A copolyimide containing alicyclic units was synthesized by two steps polycondensation reaction, from selected aliphatic/aromatic pairs of monomers.
- ✓ The morphology of this polyimide was modified into micro- and nanoparticles by reprecipitation method, using the both its structural forms, the precursor polymer, PAA, and PI respectively.

✓ *PI NPs from the PAA solution reprecipitation*

All the resulting particles presented unchanged nonporous morphologies before and after imidization, with a spherical shape having diameters in the range of 10÷700 nm, and a thermal behavior comparable to the ordinary PI NPs.

✓ *The PI Ps from PI solution reprecipitation* (were obtained by a combined method consisting of the dropwise addition of a precipitant in a PI solution and sonication, adopted in order to achieve the liquid–liquid phase separation).

- When the polymer concentration decreases (from 0.02 to 0.004 g/mL) the particles size and the systems polydispersity decrease (SEM & LLS data), while the shape changes from elliptical to spherical one (TEM results).
- The lowest polyimide concentration led to microspheres with sizes between 1.2÷3.7 µm.
- AFM measurements revealed that the formed nanopores are only superficial ones.

The partial alicyclic structure of the new obtained polyimide particles provides the perspective to develop complex performance systems expected to exhibit potential functional advantages for surface-related applications. It may be possible that the selection of a more compatible porogen with the used polyimide will allow preparing polymer particles with a higher degree of porosity suitable to be used for performant dielectric materials.

All objectives were fully realized in this stage.

Results dissemination

Original articles published in journals with impact factor

Electrical resistivity under different humidity conditions for plasma-treated and gold-sputtered, Simona-Luminita Nica, Camelia Hulubei, Iuliana Stoica, Emil Ghiocel Ioanid, Valentin Nica, Silvia Ioan, *Polym. Bull.* (2016) 73:1531–1544, DOI 10.1007/s00289-015-1560-8

Ppolyimide micro- and nanoparticles via the reprecipitation method, Camelia Hulubei, Cristina Doina Vlad, Dumitru Popovici, Iuliana Stoica, Andreea Irina Barzic, Daniela Rusu, *Revue Roumaine de Chimie*, 61(10) 2016-acceptata

Books Chapters:

Porous polymer structures by synthesis from liquid two phases systems, Camelia Hulubei, Cristina Doina Vlad in *Multiphase polymer systems: from micro to nanostructural evolution in advanced technologies*, ISBN 9781498755634 – **Editura CRC Press Taylor & Francis Group**, Editori Andreea Irina Barzic and Silvia Ioan

Viscoelastic Behavior of Liquid-Crystal Polymer in Composite Systems, Andreea Irina Barzic, Silvia Ioan, in *"Viscoelastic and Viscoplastic Materials"*,

ISBN 978-953-51-2603-4, 2016, **Publisher: InTech**, Ed: prof. Mohamed Fathy El-Amin, DOI: 10.5772/64074.

Scientific meetings: Posters

Polyimide micro- and nanoparticles via the reprecipitation method: Camelia Hulubei, Cristina Doina Vlad, Dumitru Popovici, Andreea Irina Barzic, Daniela Rusu, *12th International Conference on Colloid and Surface Chemistry*, May 16-18, 2016, Iasi, Romania, Book of abstracts: pg. 57

PATENT (Brevet OSIM): PROCESS FOR SYNTHESIS OF TRANSPARENT FLEXIBLE POLYIMIDE MATERIALS;

C Hulubei, D Popovici, M Bruma.

Patent Number: RO131123-A2; Publ. Date 30 mai 2016 (Application Details: RO131123-A2; RO000864/17.11.2014)

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