

POLYIMIDE MICRO- AND NANOPARTICLES VIA THE REPRECIPITATION METHOD

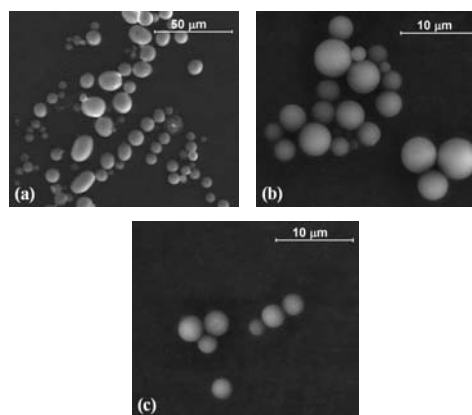
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Polymeric micro- and nanoparticles (NPs) are of broad interest in many specific surface applications including advanced materials, drug delivery, medical imaging, etc.

Here, we report the obtaining of new polymer particles based on a partial-alicyclic copolyimide (PI) derived from bicyclo [2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA). Both structural forms, the polymer precursor of PI, poly (amic acid) (PAA), and PI, were used to prepare polyimide particles (PI Ps) by reprecipitation from their solutions. Microscopy techniques, laser light scattering (LLs) and thermal analyses were used to investigate the PI Ps morphology and their thermal behavior. Microscopy data revealed a spherical shape with diameters in the range of 10÷700 nm for the PI Ps obtained from PAA solutions, and shapes like sphere, ellipse or even formless PI Ps for those prepared from the PI solution. For the last ones, spherical particle sizes range between 1÷ 13 μm . The resulting polyimide particles are thermally stable around 300 °C.



INTRODUCTION

Polymeric micro- and nanoparticles (NPs) that display microphase-separated structures are of strategic importance for applications in biomedical and microelectronic fields such as medical imaging, drug delivery, low dielectric materials, etc., as well as in fundamental studies concerning microfluidics and nanotechnology. Functional behavior of polymeric particles is strongly influenced by their shape, which has a major impact in understanding and valorizing their function. The control of size and shape is essential in the development of polymeric particles as tools and products for a variety of fields.¹

Polymer particles can be obtained by polymer synthesis from monomers using different techniques, such as suspension, emulsion or dispersion polymerization. Thus, fine polymer particles based on nonpolar monomers like styrene (ST) and divinylbenzene (DVB) or medium polar, such as methyl methacrylate compounds with reactive groups (MMA) have been well-established by the above mentioned methods.²

Complex systems with tunable surface morphology for advanced applications in microelectronics or bio-technologies require structures with performant characteristics. Among the heterocyclic polymers recognized as high performance systems, polyimides (PIs) are the

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most studied for their good combined properties including high thermal and chemical stability, high radiation resistance, high mechanical and insulating properties, and in particular, inherent high refractive index.³ PIs containing alicyclic structures are also promising candidates able to be used as substrate of flexible printed circuit or boards, insulating materials, buffer coatings in electronic packages, etc.⁴

PI-based micro- and nanoparticles have attracted more attention for their large specific surface area and excellent thermal performances useful for potential applications as high temperature thermal insulators.⁵

The PI polymer precursor, poly(amic acid) (PAA), synthesized by the polymerization of tetra carboxylic acid dianhydride with diamine, is generally well soluble in organic solvents and is easily converted into PI by thermal or chemical imidization treatment with cyclodehydration reagents.

Literature data show three main directions on getting the polyimide particles (PI Ps), namely: (1) PI Ps preparation starting from PAA solution⁶ 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;^{7,8} (2) PI Ps preparation starting from a PI solution, by the solution cooling⁹ or by the dropwise addition of a precipitant (water or ethanol) into the polymer solution^{10,11} - 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.¹²⁻¹⁴ The reprecipitation method is a convenient technique for fabricating organic and polymer nanoparticles and/or nanocrystals in a dispersion medium.^{15,16} 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.¹⁷

The present study is focused on the preparing of polyimide particles by the reprecipitation method using a soluble unsaturated polyimide (PI) derived from BOCA dianhydride. The novelty of the present work consists in the fact that, the morphology of this polyimide - used in our previous investigation¹⁸ to obtain porous

crosslinked (co) polymers as bead shape by suspension polymerization method - is now modified into micro- and nanoparticles by reprecipitation method. Both structural forms, namely the precursor polymer, PAA, and PI respectively, were used as working solutions. Polyvinyl alcohol (PVA) was chosen as porogen and polymer stabilizer. Some aspects concerning structural characterization, morphology, particle-size distribution and the thermal behavior of the obtained PI Ps are discussed.

RESULTS AND DISCUSSION

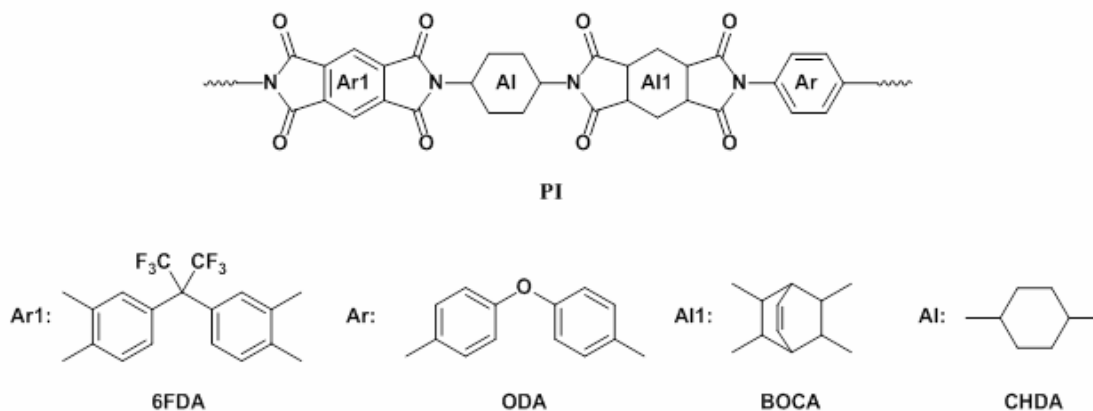
Polymer synthesis and structural characterization

The copolyimide PI was synthesized by two steps polycondensation reaction, from selected aliphatic/aromatic pairs of monomers, namely BOCA/ 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), as dianhydrides and trans-1,4-diaminocyclohexane (CHDA)/ 4,4'-oxydianiline (ODA) as diamines respectively (Scheme 1).

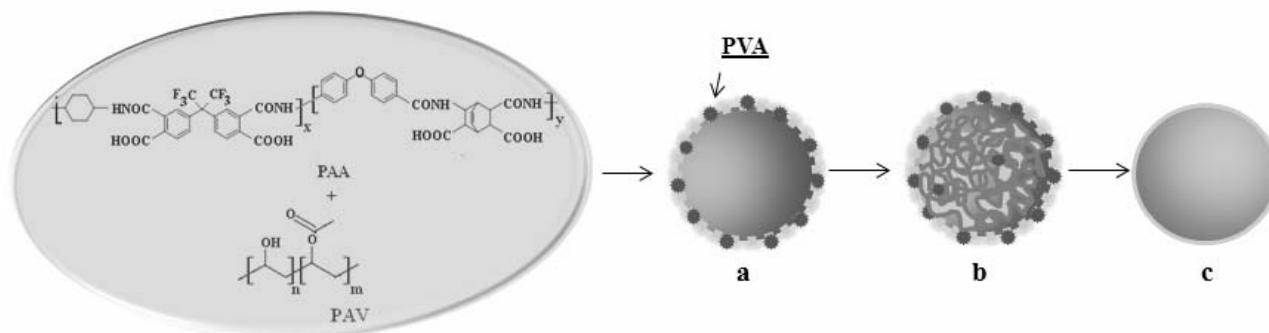
The obtained copolymer has a number-average molecular weight, M_n , of 70 000 g/mol, is thermally stable above 300 °C and is well soluble in NMP, DMAc, *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), respectively.¹⁸ Based on the synthesized polymer new particles were prepared. Their size 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.⁵

PI NPs from PAA solution reprecipitation

PAA NPs were firstly prepared by the reprecipitation from the PAA solution. The resulting PAA NPs were converted to PI NPs through chemical imidization in the dispersion medium, at room temperature, using as cyclodehydration agents acetic acid anhydride and pyridine. As good solvent, a mixture of two polar amide solvents, DMAc and NMP respectively was selected. As poor solvent cyclohexane was chosen, while as porogen, polyvinyl alcohol (PVA) was used.



Scheme 1 – The chemical structures of PI and the selected monomers.



Scheme 2 – A possible representation of the PI NPs formation.

Table 1

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 method²⁰

The initial droplets were obtained by injecting a DMAc/NMP solution containing PAA and PVA (porogen) in cyclohexane (Scheme 2). The utilized solvents, DMAc/NMP (good) and cyclohexane (poor) diffuse inside each droplet so that, the good solvent loses from its power and thus, both PAA and PVA start to precipitate forming distinct microphases, beginning with the surface layer of the droplets (Scheme 2 a, b).

The porogen chemical structure, the solubility parameter (porogen/PAA compatibility), the molecular weight and the mutual diffusion, are only some factors which decisively influence the pores formation by the porogen molecule migration inside the droplet and the microphases separation, respectively.¹⁹ Taking into account (i) the high hydrophobicity of the used copolyimide (due to its fluorinated and non-polar alicyclic units)¹⁸, (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 resulted (Scheme 2c).

All the obtained nanoparticles were spherical, with unchanged morphology before and after imidization. Having in mind the fundamental role played by the solubility parameter in a microstructure formation and taking into account the big difference between the solubility parameter of PAA and PVA used in our experiment, the obtained nonporous morphologies are explainable (Table 1). The result is consistent with the literature data which mention that a suitable porogen for such type of experiments must be qualitatively compatible with PAA by comparing the difference between the solubility parameters.²¹ The porogen molecular weight plays also an important role in this situation.²¹ The morphology of the obtained structures was analyzed using transmission electron microscopy (TEM).

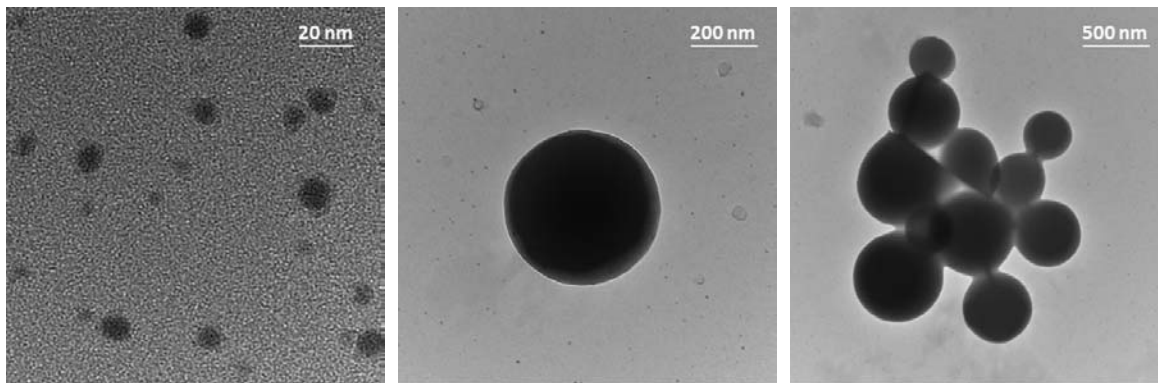


Fig. 1 – TEM images for PI NPs prepared from DMAc /NMP solution of PAA with PVA (50 wt %).

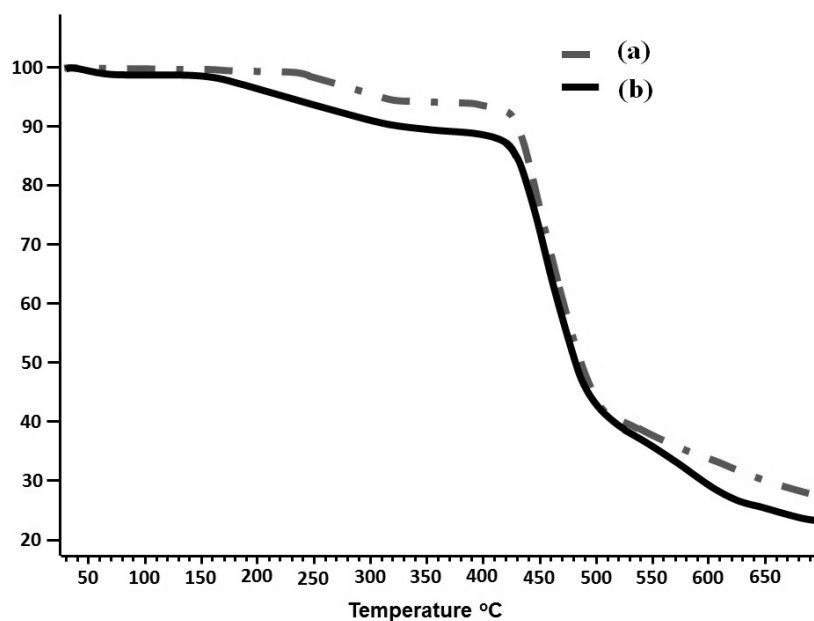


Fig. 2 – TGA (weight loss) curves for: (a) PI and (b) chemically imidized PI NPs (PVA 50 wt %).

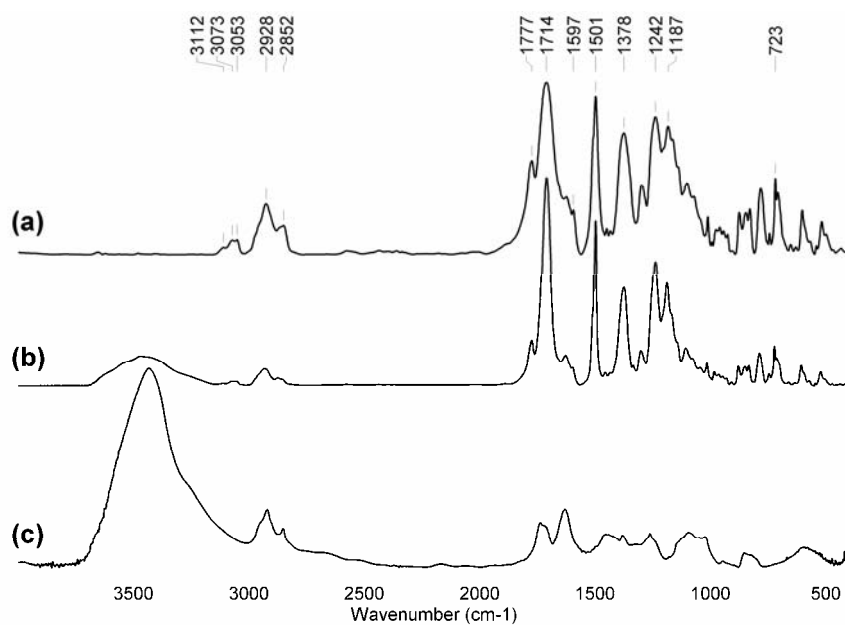


Fig. 3 – FTIR spectra for: (a) PI, (b) chemically imidized PI NPs (PVA 50 wt %) and (c) PVA.

Table 2

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

TEM images (Fig. 1) reveal that the prepared particles have a spherical shape, with diameters in the range of 10–700 nm. The TGA measurements data, displayed in Fig. 2, demonstrate that the thermal behavior of the chemically imidized PI NPs (50 wt %) - Fig. 2b - is comparable to the ordinary PI NPs with 5% weight-loss at about 275°C - Fig. 2a.

The result suggests that there is no amount of PVA inside of the particles. A similar conclusion can be detached from the FTIR analysis. Fig. 3 presents comparatively FTIR spectra for the ordinary PI nanoparticles, the chemically imidized PI nanoparticles with PVA 50 wt %, and PVA respectively.

One can observe that the 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 spectrum of the chemically imidized PI NPs structure - Fig. 3b - are similar to those corresponding to ordinary PI nanoparticles - Fig. 3a. 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), 1187 cm^{-1} (hexafluoroisopropylidene groups).

PI Ps from PI solution reprecipitation

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.

It is well known that the particle size and particle size distribution are decisively impacted by the initial drop size distribution of the polymer/water dispersion, the breakage/coalescence process²³ and the non-equal absorption of the polymer into droplets, respectively.¹⁰

In order to increase the uniformity of the drop size, the aggregation phenomenon must be diminished to decrease the coagulation. In this

respect we used two methods: (i) the adding of the precipitant solution into the polymer solution to obtain the “liquid–liquid demixing” effect¹⁰ and (ii) the using of PVA as polymeric stabilizer, able to act as protection against the collision and aggregation of the droplets.

To ensure a continuous and complete precipitation in system, the precipitant was added and after the beginning of the phases separation. A larger quantity of precipitant provides better droplets isolation and facilitates solvent removal. The particles shape and size are dependent on the system conditions, especially on the polymer and stabilizer concentration. Table 2 shows the experimental conditions for the particles preparation.

In Fig. 4 are displayed some morphological aspects of the microparticles surface investigated by atomic force microscopy (AFM).

Height and corresponding amplitude images (which provide complementary information on topography by additional contrast of edges) highlighted the existence of microparticles with a relative spherical shape (sometimes ellipse or formless) and an average diameter of $12.28 \pm 1.75 \mu\text{m}$. At a closer look, 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 in Fig. 4, 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 $f_{\text{shape}} = 1.21 \pm 0.35$, using the pore area A and perimeter, P ($f_{\text{shape}} = 4\pi A / 1.064 P^2$)¹⁸ one 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} ($f_{\text{elong}} = d_{\text{min}} / d_{\text{max}}$)²⁴. The average elongation factor close to 1 ($f_{\text{elong}} = 0.89 \pm 0.11$) describes an almost circular contour of the pores. All the mediations were performed on 10 arbitrary selected particles.

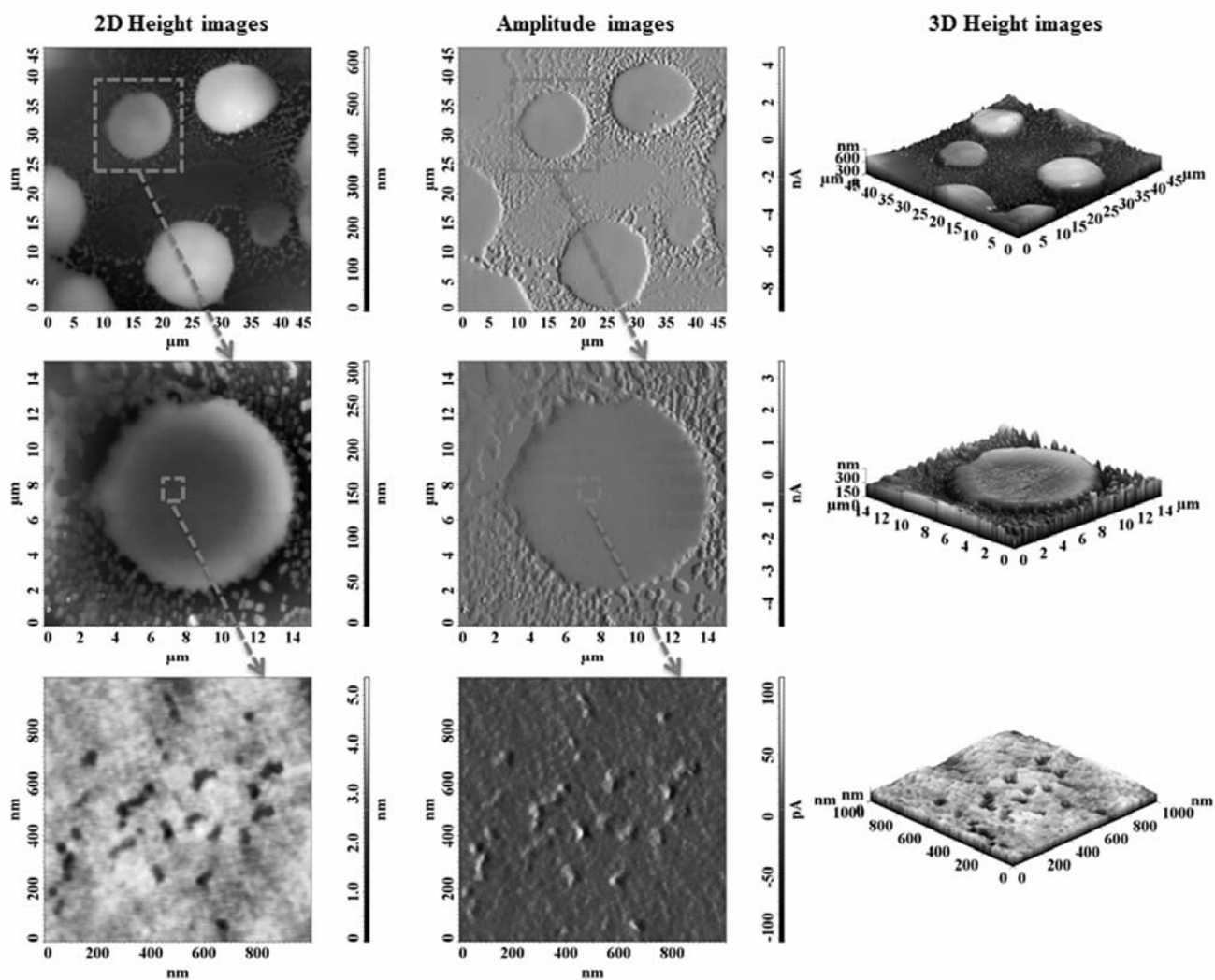


Fig. 4 – Height and corresponding amplitude AFM images of the microparticles surface on different scan sizes for the PI Ps (a) sample.

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) – Fig. 5a – to spherical one – Fig. 5b,c – while the

their size decreases. For the lowest polyimide concentration, microspheres with sizes between 1.2–3.7 μm were obtained. Fig. 5 presents some illustrative scanning electron microscopy (SEM) images of the resulting PI particles.

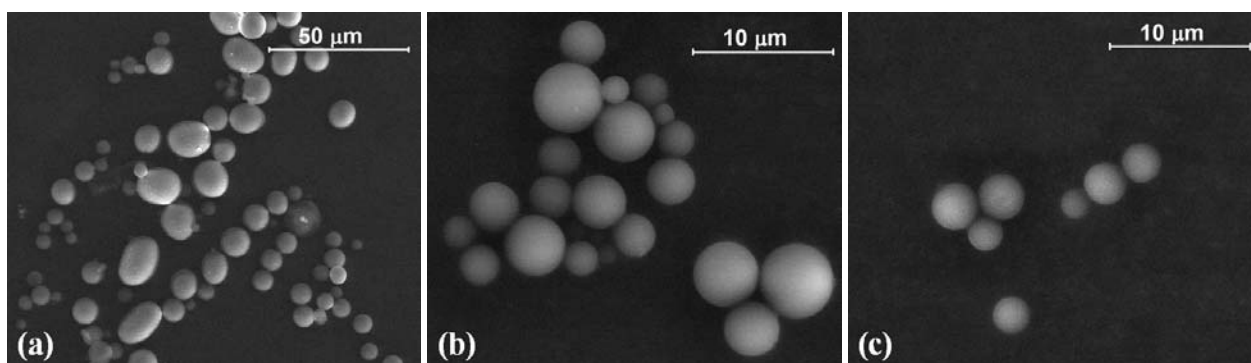


Fig. 5 – SEM images for the samples: PI Ps (a), PI Ps (b) and PI Ps (c).

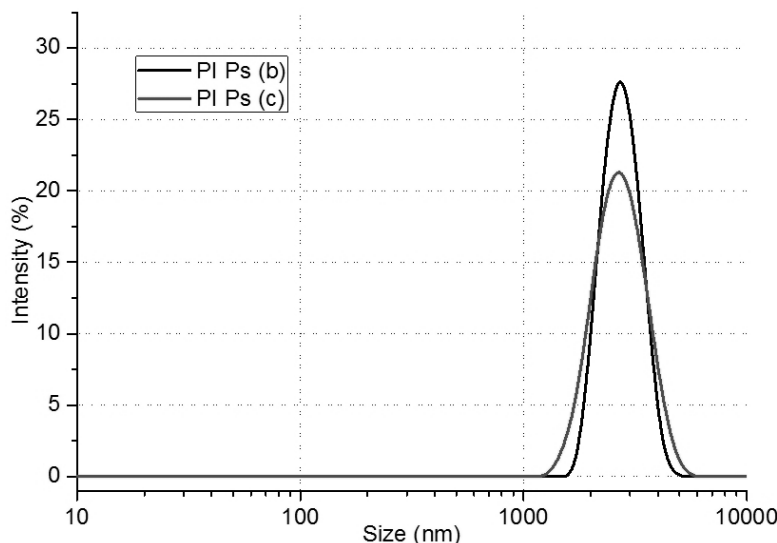


Fig. 6 – Particle size distribution for the systems noted PI Ps(b) and PI Ps(c) from Table 2.

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 3030–2770 nm (Fig. 6).

This could be associated with the fact that the stabilizer concentration practically does not influence the number of 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.¹⁰

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.

EXPERIMENTAL

Materials. High purity chemicals from various commercial sources: bicyclo [2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA), 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), 4,4'-oxydianiline (ODA), *trans*-1,4-diaminocyclohexane (CHDA), poly (vinyl alcohol) 88 % PVA grade (Mw 150,000), 1-methyl-2-pyrrolidone anhydrous (NMP), *N,N*-dimethylacetamide (DMAc), methanol, acetic anhydride and pyridine were used as received.

Polymer synthesis. The polymer containing alicyclic units was prepared by the solution copolycondensation reaction of two selected dianhydrides, BOCA and 6FDA, with the diamines, ODA and CHDA (equimolar ratio between the amine and anhydride groups), using NMP as solvent, under nitrogen atmosphere. The obtained polyimide precursor,

namely the poly(amic acid) (PAA), was further transformed by thermal treatment for 6 h at 185°C, into the corresponding PI structure. The reaction mixture was precipitated in water, the resulting polymer was filtered, washed with water and methanol, and dried for 8 h at 105°C. The details of reaction steps were reported in other works.¹⁸

PI Ps from PAA solution reprecipitation. A solution of DMAc/NMP (1:1 molar ratio) - good solvent - containing PAA and porogen (PVA) was prepared as follows: a given amount of DMAc/NMP solution containing the porogen (1 wt %) was added to a DMAc/NMP solution containing PAA, so that the concentration of PAA in the final solution to be 1.5 wt %; the porogen concentration in system was 25% and 50%, respectively. In a typical example: 100 μ L DMAc/NMP solution containing PAA and porogen were injected with a microsyringe, into 10 mL cyclohexane - poor solvent - at room temperature, under sonication. After 1h, the obtained PAA NPs were chemically imidized by injecting of 100 μ L pyridine/acetic anhydride mixture (1:1 molar ratio) into the resulting dispersion. Finally, the prepared PI NPs were separated by centrifugation and dried under vacuum.

PI Ps from PI solution reprecipitation. A first DMAc solution (I) containing PI (0.02 g/mL) and PVA (0.02 g/mL) respectively was prepared. A sample of 100 mL of this solution was placed into a bottle in an ultrasonic bath and a second PVA (0.02 g/mL) water solution (II) was dropwise added at 80 °C, so that the second drop was added only when the precipitate caused by the first drop almost disappeared. The ratio between the added solution II to the solution I was 2/1 v/v %.

The suspension was sonicated for 2 hours. The microparticles were collected by filtration, washed many times with water to remove DMAc and PVA, and dried in a vacuum oven.

Characterization

Infrared spectra (FTIR) were obtained with a Bruker Vertex 70 spectrometer in transmission mode, at 24 cm^{-1} resolution, by using precipitated polymer grounds in potassium bromide pellets.

Polymer solubility was determined at room temperature at a concentration of 1 % (w/v).

Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere at a heating rate of 10 °C/min from 25 to 700 °C with a Mettler Toledo model TGA/SDTA 851. The initial mass of the samples was 2–5 mg.

Transmission electron microscopy (TEM) micrographs were recorded with a Hitachi High-Tech HT7700 microscope working at 120 kV.

Environmental Scanning Electron Microscope (ESEM) type Quanta 200 was used to analyze polymer beads morphology.

Atomic force microscopy (AFM) measurements were performed on a SPM SOLVER Pro-M platform (NT-MDT, Russia) at room temperature in semi-contact mode, using a commercially available cantilever NSG 10 (NT-MDT, Russia) with a probe tip radius of 10 nm.

The particle size distribution was determined with a dynamic light scattering technique (Zetasizer model Nano ZS (Malvern Instruments, UK)) with laser working at 633 nm (He/ Ne). A non-invasive back scatter (NIBS) technology is used, wherein the optics are not in contact with the sample, back scattered light being detected. The NIBS technology reduces multiple scattering effects so that size distributions in higher concentrations of sample can be measured. This system allows the application of the Mie method over the whole measuring range, from 0.6 nm to 6 μ m.

CONCLUSIONS

A copolyimide containing alicyclic units was synthesized by a two step 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.

The PI NPs were obtained 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 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 μ m. 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.

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