



Host Institution:

PETRU PONI Institute of Macromolecular Chemistry of Romanian Academy
41-A, Grigore Ghica Voda Alley, 700487 Iași, Romania

Contracting Authority:

Executive Unit for Financing Higher Education Research Development and Innovation, Romania

EXPLORATORY RESEARCH PROJECT

PN-II-ID-PCE-2011-3-0937

Contract nr. 302/05.10.2011

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

- 2015 -

Research Team:

CSII Cristina Doina Vlad

CSII Camelia Hulubei

CS Irina Barzic

CS Anca Filimon

AC Iuliana Stoica

AC Dumitru Popovici

Tehn. Ioan Tescu

Project leader

CSI Silvia Ioan

BRIEF REPORT
concerning the results obtained by the project team between 16
December 2014 – 15 December 2015

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

Associated Activities:

1.1 The obtaining of a functional polymer containing alicyclic groups as crosslinked porous beads forms for potential utilizable as high-temperature nano-containers

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

1.1. The obtaining of a functional polymer containing alicyclic groups as crosslinked porous beads forms for potential utilizable as high-temperature nano-containers

Crosslinked (co) polymers in beads form A functional polymer can be obtain both by copolymerization and by post-functionalization.

The introduction of polar functionalities in a polymer chain can induce different properties such as hardness, flexibility, impact resistance, resistance to cracking, gas impermeability, adhesion, miscibility, etc.

Table 1. Materials used in the copolymers synthesis

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. =
N-carboxyphenyl maleimide	synthesized	CPMI	Recrystallization from ethanol
monoethylene glycol dimethacrylate	Aldrich	MEG	Used without purification
<i>trans</i> -1,4-cyclohexan-diamine	Aldrich	CHDA	Recrystallization from <i>n</i> -hexane; p.t. =
<i>N</i> -methyl-2-pirolidone	Aldrich	NMP	Vacuum distillation at 10 mmHg, dried on CaH ₂ , stored on 4 Å molecular sieves
1,4-Dioxane	Aldrich	Dx	Used without purification
Benzyl alcohol	Aldrich	BzOH	Used without purification
polyvinyl alcohol	Aldrich	PVA	Used without purification

Synthetic Method: crosslinked (co) polymerization

Technique work: suspension polymerization (PSP)

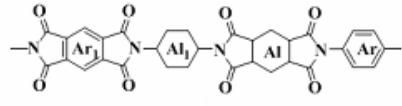
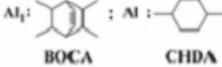
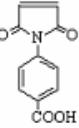
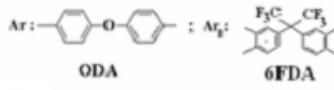
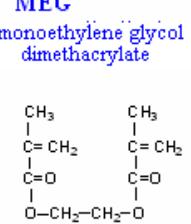
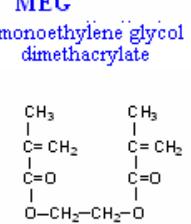
PSP involves using a system where the mixture of "monomers" containing free radical initiator is dispersed by mechanical stirring in drops form - the discontinuous phase- in a liquid phase – the continues phase – where the drops polymerize.

The drops adopt a spherical shape for a maximum stability (minimum interfacial energy), their average size being controlled by a number of factors among which, really important are stirring speed, quantity and quality stabilizing agent respectively.

Were studied two reaction systems (1 * and 2 *) which use the same copolyimide structure, CPI, but, different crosslinker, namely:

- *N*-carboxyphenyl maleimide, CPMI (system 1 *) - maleimide type crosslinker: by its carboxylic functions can sensitively change the polymer properties, or can serve as attachment sites for other functional units;
- Monoetilegligol dimethacrylate MEG system (2 *) – methacrylic esters type crosslinker, with polar (hydrophilic) structure.

Table 2. Reaction systems used in the synthesis of crosslinked bead polymers

Reaction system	Reagents		Porogens	Dispersion medium	Stabilizer
	Copolyimide CPI	Crosslinker monomer			
1*		CPMI N-carboxyphenyl maleimide	NMP/BzOH mixture : 1 / 3	water	PVA / CaCl ₂
1*	 unde:  				
2*			NMP/DMAc/BzOH mixture : 1/1,25/1,5	water	PVA / CaCl ₂
2*	BOCA - Bicyclo[2.2.2]-7-octene-2,3,5,6-tetracarboxylic dianhydride 6FDA - 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride CHDA - trans-1,4-cyclohexan-diamine ODA - 4,4'-oxydianiline				

Statistical copolyimide (CPI)

CPI: Mn= 70000 g/mol. ; Td> 400 °C;

The polymer is soluble in dipolar aprotic solvent (NMP, DMAc, DMF, DMSO at room temperature) and the in Dx at heating.

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](#).

N-carboxy phenyl maleimide (CPMI)

N-carboxy phenyl maleimide monomer, CPMI was obtained by a polycondensation reaction in two steps, in agreement with the method reported by Searle. The first step is the reaction of maleic anhydride and *p*-amino benzoic acid in anhydrous acetone at room temperature, the second stage being the chemical cyclodehydration of the resulting poly (amic)acid, by using sodium acetate and acetic anhydride.

Elemental analysis (%): Calc. for C11H7NO4 (217.17): C, 60.83; H, 3.25; N, 6.45. Found: C, 60.48; H, 2.84; N, 5.97.

IR (KBr) cm⁻¹: 3600-2700 (broad OH), 1777 (C = O imide I), 1710 (imide I), 1600, 1510 (C = C, aromatic), 1390 (imide II), 1215 (CO, COOH) 1145 (imide III), 820 (*p*-disubstituted aromatic ring), 690 (imide IV). *¹H-NMR (DMSO-d₆, ppm)*: 12.36 (s, 1H, COOH), 7.93 (d, 2H, ortho to -COOH), 7.49 (d, 2H, ortho to -N <), 7.15 (s, 2H, olefinic).

The suspension polymerization of CPI was performed using

- different molar ratios of polymerizable compounds:

system 1*: CPI / CPMI (25/75, 40/60, 50/50, 60/40)

system 2 * CPI / MEG (25/75, 40/60, 50/50, 60/40)

- porogen mixture:

system 1 *: NMP / BzOH: 1/3

system 2 *: NMP / DMAc / BzOH: 1 / 1.25 / 1. The same conditions for stabilization;

Example of Synthesis

The organic phase contains a mixture of the crosslinkable compounds, CPI / CPMI, dissolved in a mixture of solvents, NMP / BzOH, at 55 °C, when the initiator is added.

The dispersion medium: contains water, PVA and CaCl_2 (PVA is dissolved in water at 80°C for 2 hours, after that it is let to cool). Separately CaCl_2 solution is made by dissolving it in cold water.

Finally the two solutions are mixed to form the dispersion medium necessary.)

The organic phase in its homogeneous and transparent form, was poured into the dispersion medium from the reaction vessel, at 55 ° C. The polymerisation process takes place under stirring, for 5 hours at 60 ° C and 15 - 25 hours at 80 ° C until the (co) polymer crosslinks.

Finally, the polymer particles are washed several times with boiling water and centrifuged at 2000 rpm., after which the medium is extracted with inert media in Soxhlet and dried in vacuo.

Spectral characterization

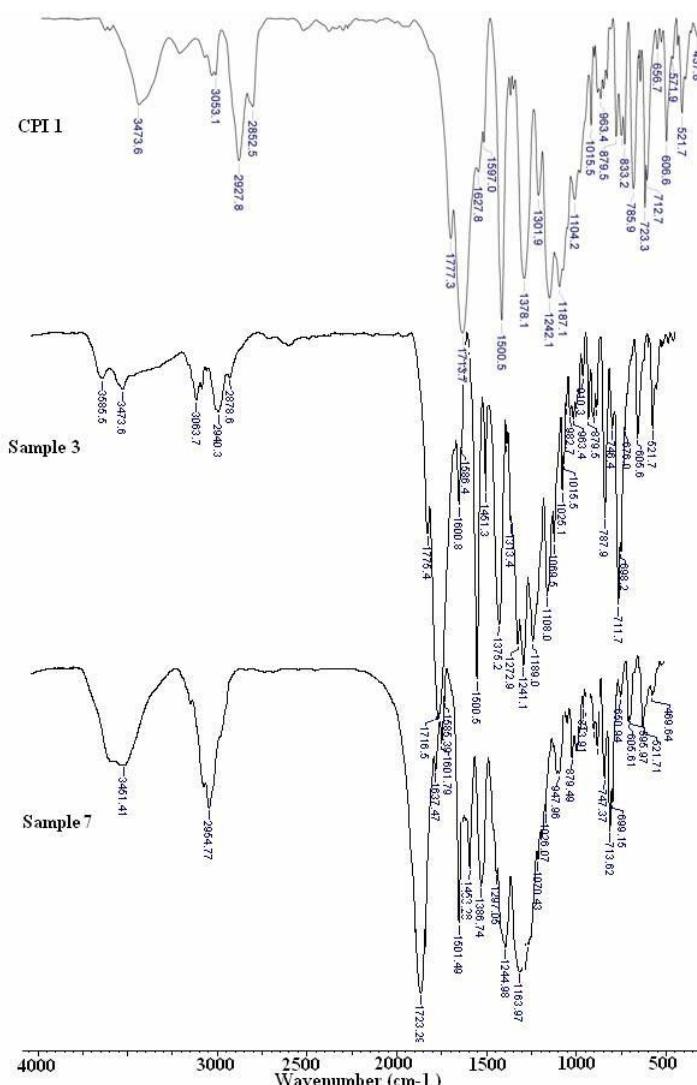


Figure 1. FTIR spectra for CPI, 3 and 7 samples

FTIR spectra of the CPI and the crosslinked polyimide samples confirm:

- Imide structure - absorption peaks:

* About 1775 cm⁻¹ and 1710- 1723 cm⁻¹ (symmetrical and asymmetrical stretching vibration of the C = O in the ring imide); * at 1378 - 1386 cm⁻¹ (the extent of the link CNC); * at approximately 723 cm⁻¹ (imide ring deformation);

*Aromatic structure - absorption peaks at about 1500 cm^{-1} (CH), at $3063\text{-}3033\text{ cm}^{-1}$ (CH) associated with the benzene ring;

**Aliphatic structure* - the absorption peaks at 2954 and 2852 cm⁻¹ associated with the link CH₂ of the aliphatic units.

Porous beads formation mechanism

The formation mechanism of water-insoluble monomer suspensions is illustrated schematically in Figure 2. The bead formation mechanism

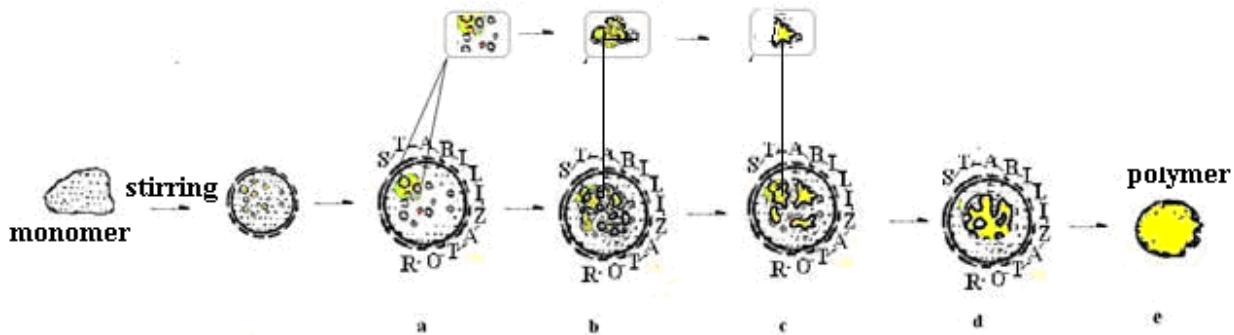


Figure 2. A possible suspension polymerization mechanism for the of water-insoluble monomers

The radical crosslinking (co)polymerization (CRR) has some specific behaviors, the process of initiation of increasing chains, which causes morphological differences for the resulting crosslinked structures, being fundamental.

The encircling of the monomer droplet with a stabilizer layer (Figure 2) controls and reduces the coalescing process, helping to stabilize the monomer droplet size. The copolymers obtaining from mono- and polyunsaturated monomers, by the CRR mechanism assumes that, at the beginning of the (co) polymerization reaction, polyfunctional linear macromolecules that remain dissolved in monomers (Figure 2a) are formed.

While the polymerization progresses, the insoluble polymer granules which constitute the "centers" or "nucleus" of polymerisation (Figure 2b) occurring. The polymerization continuing leads to the increase of the polymerization centers, the pellets become sticky, bind to each other (Figure 2c), the particle begins to contract; the monomers polymerization continues according to the mechanism required by the type of monomers, a solid phase (Figure 2d) which in certain conditions, can contain pores, forms. On measure the polymerization progresses, the monomer consumes, the surface pores block while those from inside close, resulting a polymer in bead form

The polymerization temperature depends on the nature of the initiation system, and it should not exceed the decomposition temperature of the initiator. To finalize the crosslinks that form the heterogeneous network of beads, the temperature and the reaction time are dependent on the quantity and quality of the starting material.

Factors influencing the formation of crosslinked porous structures in the bead shape

The beads formation imposes some essential conditions:

- obtaining of uniform monomer droplets suspension in aqueous phase;
- reducing of the droplets coalescence during polymerization.

A stable dispersion of droplets in the continuous phase is provided by stabilization and stirring. The most important factor affecting the polymerization in suspension is the suspension stabilizer

Stabilizer effect

In the present study, two kinds of polyvinyl alcohol (PVA) of different molecular weights and hydrolysis degree were used as stabilizer (PVA: Mw = 146000 / 99% hydrolyzed; Mw = 88 000 / 88% hydrolyzed). For both reaction systems the results show that, the polyvinyl alcohol with very high hydrolysis degree (99%, Mw = 146,000) generates systems less stable compared to that having a degree of hydrolysis below (88%). Figure 3 shows several images regarding the influence of the suspending agent quality on the reaction system stability.

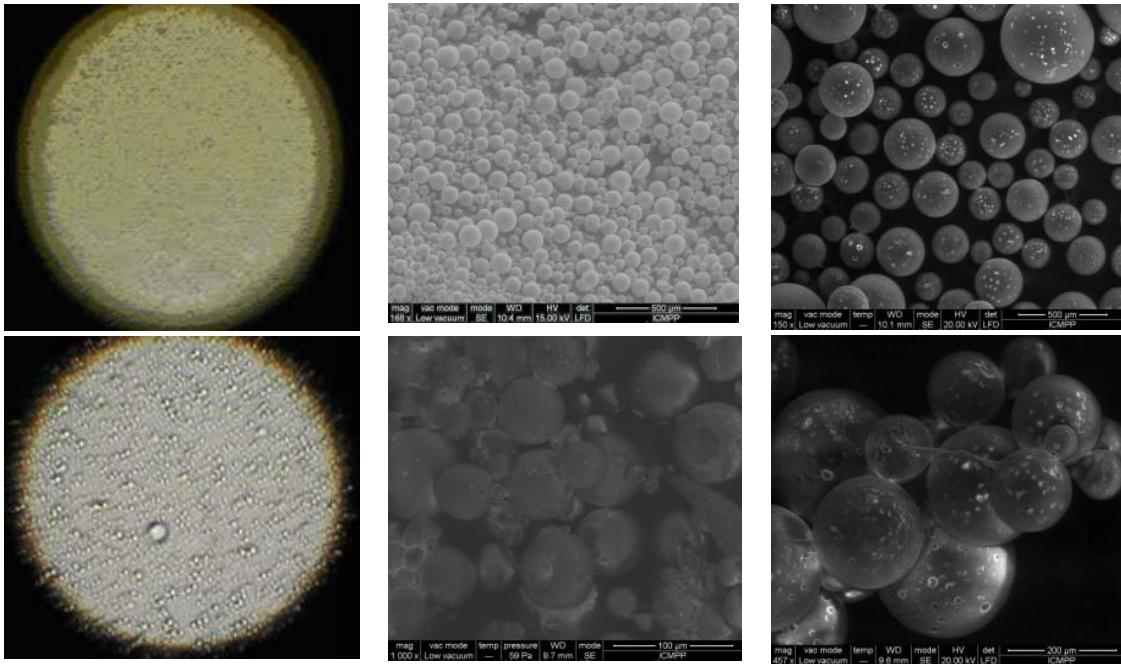


Figure 3. Effect of the quality suspending agent system on the system stability
: (a) PVA Mw = 146000/99%; (b) PVA Mw = 88 000/88%

A system with good stability of the dispersion shows small droplets, due to the interfacial tension which provides the necessary balance between the breaking/coalescence rate of the droplet. The stability of the dispersion reaction system involves several factors, namely:

- *the balance of polarity* - hydrophil/hydrophob - of the studied polymerization mixture

(CPMI- monomer with a strong polar nature (hydrophilic) and CPI- polymer with a pronounced hydrophobic character, due to the non-polar alicyclic sequences and the 6F bridge from the polymer chain structure);

- *the stabilizer hydrolysis degree (PVA)*

(affects the hydrophobicity, conformation, and the surface activity of the PVA at the interface of monomer / water, by default, the suspension stability and thus, the droplets average size)

- *the stabilizer molecular weight*

(PVA having Mw = 88 000 acts more efficient as stabilizer compared to PVA Mw = 146,000, due to an area more active at the droplets interface and also, to its less hydrophilic character (hydrolysis degree of 88 %) which allows to adjust the particles size by a better positioning on their surface).

In conclusion: PVA Mw = 88 000 achieves a stable suspension, inhibits the droplets coalescence, forms a resistant mechanical film at the monomer / water interface, ensuring the optimal growth of the viscosity and a good dispersing of monomers.

Diluents effect

In the crosslinking polymerization the monomers act as diluents, the phase separation and thus the resulting polymer morphology structures essentially depending on their quantity and quality. Diluents, also known as porogens, can be: solvent or non-solvent for the polymer chains, linear polymers, or mixtures thereof.

They determine the formation of permanent heterogeneous structures (which can contain pores after drying) with the role to remain in the crosslinked formed beads. After the polymerization completion, the pore-forming is removed, the sites occupied by this practically becoming "pore" structure in question. The samples summarized and shown in Tables 1 and 2 were stabilized with PVA having a hydrolysis degree of 88% and Mw = 88,000. From Table 1 it is noted that the crosslinker monomer CPMI leads to crosslinked structures only if it is in a ratio of 50 -60% in the reaction system (samples 2, 3), unlike in the case when crosslinker is MEG (Table 2).

Table 1. Reaction system for the poly (CPI1 –co- CPMI) preparation

Cod	CPI%	CPMI%	NMP : BzOH	Obs.
1	25	75	1 : 3	without crosslinking after 48 h
2	40	60	1 : 3	crosslinking after 24 h
3	50	50	1 : 3	crosslinking after 22 h
4	60	40	1 : 3	without crosslinking after 48h

Table 2. Reaction system for the poly(CPI1 –co- MEG) preparation

Cod	CPI%	MEG %	DMAc : BzOH : NMP	Obs.
5	25	75	1,25 :5 : 1	14 h crosslinking
6	40	60	1,25:1,5 :1	18 h crosslinking
7	50	50	1,25:1,5 :1	25h crosslinking
8	60	40	1,25:1,5 :1	25 h crosslinking

The synthesis changes its composition throughout the polymerization, such as solubility parameter will change permanently. Pore size distribution will depend on the momentary value of the solubility parameter of the solvent- polymer.

The solubility parameter of the initial polymerization mixture (δ_m) was calculated using the formula:

$$\delta_m = \frac{\delta_1 M_1 X_1 + \delta_2 M_2 X_2}{M_1 X_1 + M_2 X_2}$$

where the index 1 relates to monomer and the index 2 refers to the porogen medium used in synthesis (δ - solubility parameter; M - molecular weight; X - mole fraction used in synthesis).

Table 3. Solubility parameter values of the components used in synthesis

Porogen	δ (MPa ^{1/2})	Molecular weight	Density (g/ml)
BzOH	23.8	108.14	1.044
NMP	22.9	99.14	1.028
1,4 Dx	20.5	88.11	1.033
CPI	24,04	1828	1,204
MEG	18.81	198,22	1,05
CPMI	17,33	217	1,5

For the preparation of copolymers according to the Tables 1 and 2, the solubility parameters values of the used porogen mixtures were calculated with the formula:

$$\delta_m = \sum \frac{\delta_1 M_1 X_1 + \dots + \delta_n M_n X_n}{M_1 X_1 + \dots + M_n X_n}$$

Where δ - solubility parameter; M - molecular weight and X - porogen mole fraction of the original mixture used in synthesis.

According to the results presented in Table 4, there is a very good compatibility between:

- the solubility parameter values of the polymerizable mixture (23.55) and porogen respectively (23,59) ($\delta_{mix} = \delta_{por} - 0.04$) - sample 2, system **CPI / CPMI**;

and also for

- the solubility parameter value of the polymerizable mixture and porogen / sample 6, system CPI/MEG ($\delta_{\text{mix}} = \delta_{\text{por}} + 0,07$)

Table 4. The solubility parameter values (porogen, polymerization mixture) in the reaction systems

Sample	Porogen mixture	Polymerizable mixture		
poly(CPI –co- CPMI)	NMP/BzOH: 1/ 3 ($\delta_{\text{por}}=23,59$)	CPI/CPMI Sample Cod 1 2 3 4	Molar ratio 25/75 40/60 50/50 60/40	δ_{mix} 22.98 23.55 23.34 23,56
	NMP/DMAc/BzOH: 1/1,25/1,5 ($\delta_{\text{por}}=23,23$)	CPI/MEG Sample Cod 5 6 7 8	Molar ratio 25/75 40/60 50/50 60/40	δ_{mix} 22,76 23,30 23,52 23,68

Morphological aspects

In favorable thermodynamic conditions porous structures with high specific surface area can be obtained. Table 5 shows morphological characteristics [porosity (P), pore volume (V_{por}), specific surface area (S_{sp}), bulk density (D_{ap})] for some of the synthesized samples.

Table 5. Morphological characteristics for some of the synthesized samples

Sample	P	V_{por}	S_{sp}	D_{ap}
2*	71.03	1.69	360	0.3733
3*	43	0.5	298	0.7099
6**	38,87	0.48	352	0.7455
7**	73,93	2.30	195	0.3179

*poly(CPI –co- CPMI) ; ** poly (CPI –co- MEG)

It is found that the specific surface area for both systems, **poly (CPI CO- CPMI)** and **poly (CPI CO- MEG)** attains a maximum value for the CPI / crosslinker molar ratio: 40/60 (samples 2, 6, Table 5).

The total pore volume (VP) was determined according to the equation:

$$VP = V_{\text{por}} / M_{\text{pearl}} = V_{\text{sp}} - V_{\text{ap}} / 1 = 1/D_{\text{ap}} - 1/D_{\text{sp}}$$

The samples porosity (P) means the pore volume contained in an amount "m" of pearls on the total volume occupied by pearls:

$$P = V_{\text{por}} / V_{\text{pearls}} = (V_{\text{ap}} - V_{\text{sp}}) / V_{\text{ap}} = 1/D_{\text{ap}} - 1/D_{\text{sp}} = 1 - D_{\text{ap}}/D_{\text{sp}}$$

The samples porosity depends on the pore size and the pore diameter (2r), being inverse proportion to the specific surface area according to the equation:

$$2r = (4VP / S_{\text{sp}}) 10^3 \text{ nm}$$

Optimization of morphology

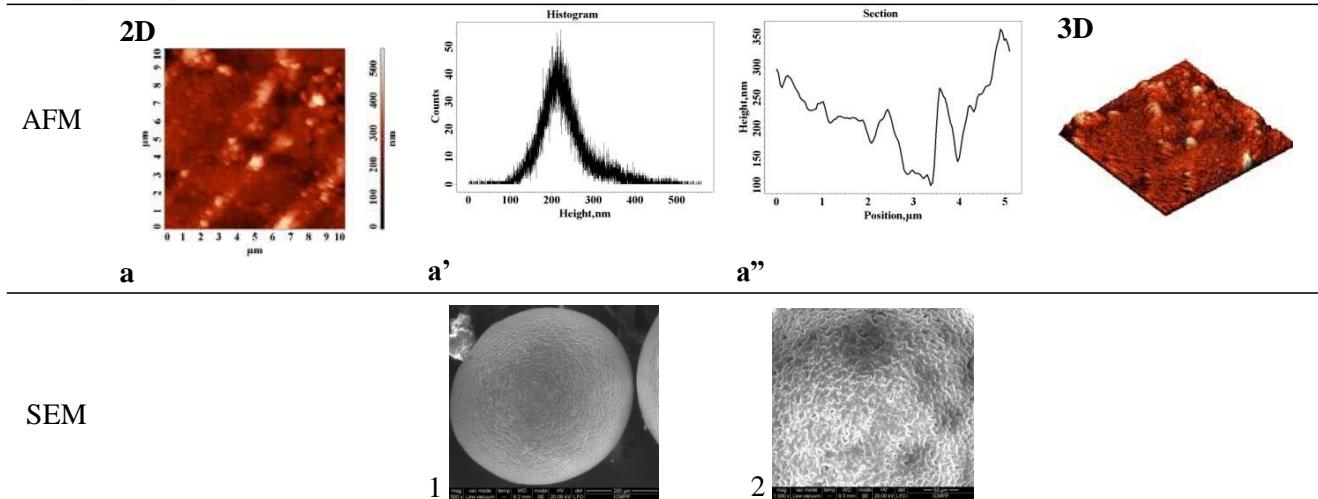
The morphological characterization of the synthesized samples was performed with specific equipment for high precision optical measurements, atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

AFM analyses confirm formation mechanism of the crosslinked polymers, for the first time proposed by Kun and Kunin and developed by Dusek as: (1) the production and agglomeration of highly crosslinked gel microspheres, (2) the binding together with agglomerates and the matrix structure fixation.

From this perspective, the bead porosity is the result of the phase separation which occurred during polymerization in the porogen presence.

Optical microscopy analysis (AFM, SEM)

Sample 3 [poly (CPI –co- CPMI)]



Sample 7 [poly (CPI –co- MEG)]

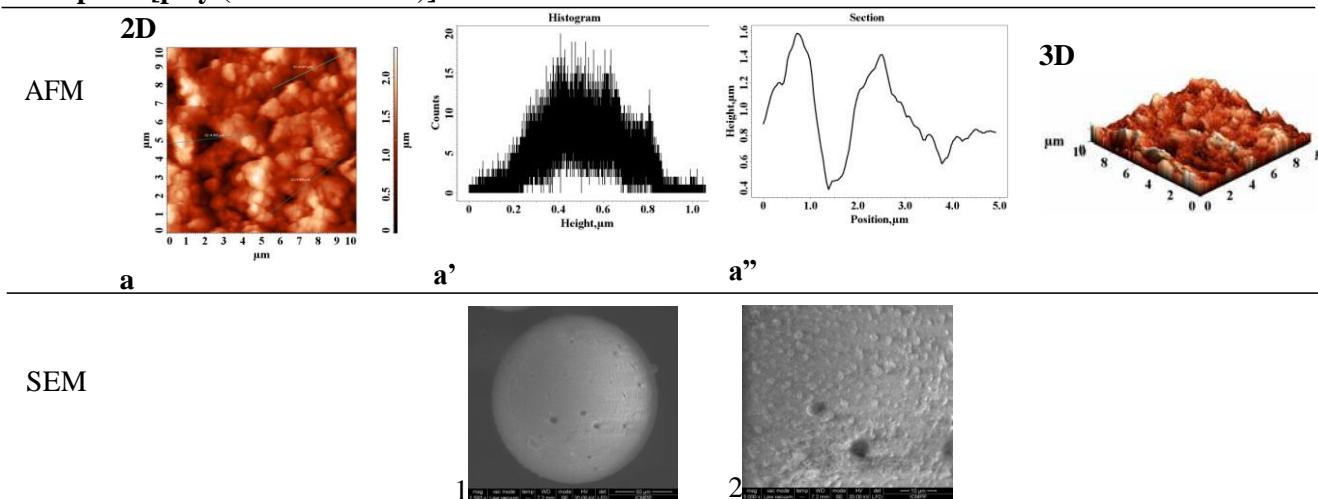


Figure4. Microscopic analysis 2D AFM height images (a, b), crosssection profile taken along the line from 2D image (a', b') and height histogram with 3D image (a'', b'') as inset of crosslinked microbeads surfaces of samples no. 3 and 7; SEM images: 1 external surface bead; 2 internal structure.

The submicroscopic particles formation depends on the thermodynamic quality of the reaction mixture causing a different ordering of the structural edifice.

The quantity and quality of the inert medium influence the final product characteristics.

The inert medium does not change the network crosslinking degree, but changes the porous structure formation mechanism. The solvation conditions that appear in system during the crosslinking, depend on the solvent-polymer interactions..

Polymeric nanocapsules

All the three states of matter (solid, liquid, gas) can be micro-encapsulated. Polymer microcapsules have diameters between 1 and 20 mm, and are recognized as transportation systems for any of these types of materials. The microcapsules are fine spherical particles having

*- *homogenous or monolithic* structures (microspheres) in which the active substance is dissolved or dispersed throughout the polymer network, or

*- *reservoir* structures (microcapsules) in which the active substance is surrounded by the polymer matrix.

The microcapsules structure is very diverse and generally depends on the used technology. Nanospheres are submicron particles, morphologically equivalent with the microspheres and microcapsules, respectively, but due to their smaller size, they have a high potential for use. The fact that the beads are crosslinked structures, chemically, thermally and mechanically resistant, justifies the purpose to obtain functionalized polyimides as beads, potential usable as micro- or nanocontainers for high temperatures. The selection and the use of polyimides as polymer support are justified by their favorable balance of properties related to the high thermal, chemical, oxidation and radiation stability, mechanical strength and good dielectric properties (dielectric constant small, high resistivity).

The introduction of specific functional groups (COOH, COO) in the polymer structures allows adjusting the properties in order to obtain polymeric nano- and microcapsules adapted for various applications. The synthesis of nanocapsules from the copolyimide, CPI, and the crosslinkers CPMI or MEG, respectively, is a novelty, the resulting nanospheres being potential usable in microelectronics.

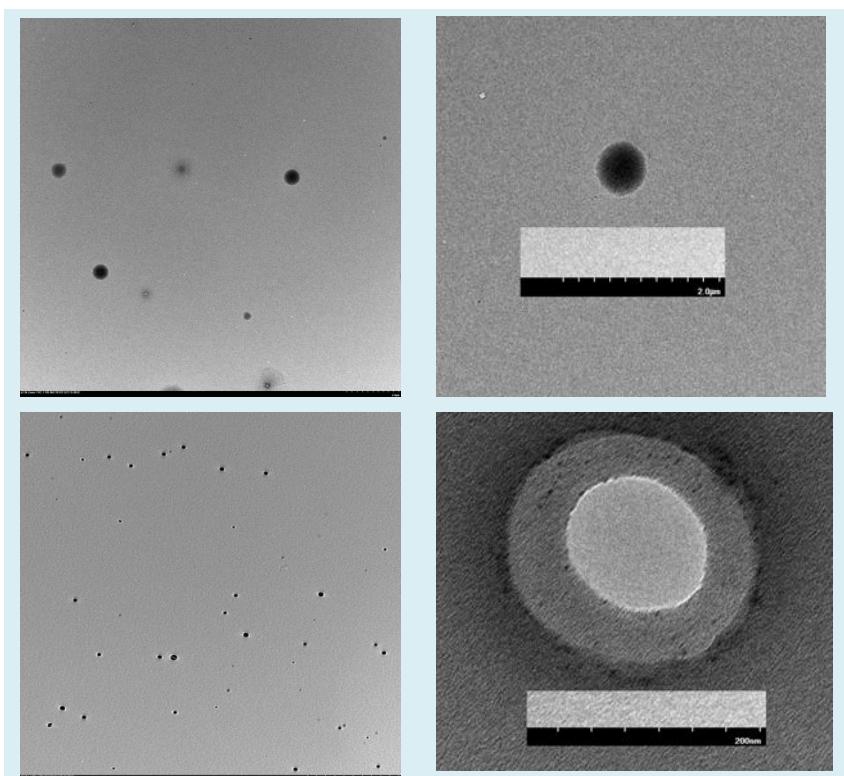


Figure 5. TEM images for: a) **poly (CPI-co-MEG)** (CPI/MEG=1/1; diluents media DMAc, BzOH, NMP)
b) **poly (CPI-co-CPMI)** (CPI/CPMI=1/1); diluents media BzOH, NMP)

The preparation technology of this polymeric systems, modified as compared to the classic recipe will be patented.

Swelling properties.

Table 6 presents the solvent retention coefficient for the functionalized samples 3, 2, 7, 6, as compared with two unfunctionalized samples, 3.I & 4.I selected from a previous study of the same project (stage 2014, “*New polyimide-based porous crosslinked beads by suspension polymerization: physical and chemical factors affecting their morphology*” [J Polym Res, 21\(9\), 2014, DOI:10.1007/s10965-014-0514-4](https://doi.org/10.1007/s10965-014-0514-4)).

The swelling degree (**B**) in water and methanol was measured at equilibrium and calculated using the formula:

$$\mathbf{B} = (\mathbf{V}_s - \mathbf{V}_d) / \mathbf{V}_d \times 100\%$$

where Vs and Vd are the copolymer volumes, swollen and unswollen respectively.

The weight of the retained solvent (**W**) was estimated with the relationship:

$$\mathbf{W} = (\mathbf{W}_s - \mathbf{W}_d) / \mathbf{W}_d$$

Table 6. Retention and swelling coefficient

Sample	Crosslinker	B%	Wg/g In water	B%	Wg/g in methanol
3.I	35 BMI	34	1.28	106	0.77
4.I	40 BMI	67	1.48	195	1.03
3	50 CPMI	62	1.44	183	1.34
2	60 CPMI	69	1.50	215	1.82
7	50 MEG	73	1.81	302	2.31
6	60 MEG	77	1.93	346	2.49

The functionalization determined the sensitive increase of the solvent retention properties.

Thermal degradation

The thermal decomposition of the crosslinked functionalized polymer depends on the synthesis reaction parameters (nature and quantity of the co-monomers, the existence of functional groups, temperature, initiator, etc.). The degradation stages number, the weight loss and other kinetic parameters resulted from the thermogravimetric study, show the complex mechanism that characterizes the thermal reactions of the crosslinked polymers.

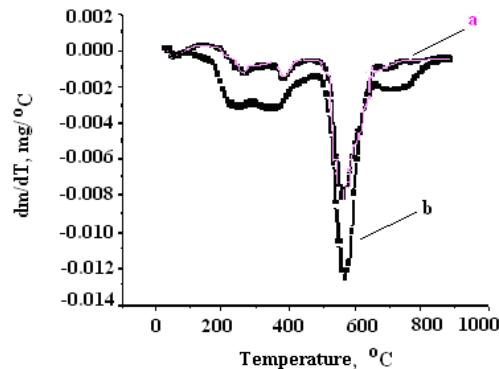


Figure 6. Thermogravimetric curves (TG): (a) poly (CPI-co-MEG); (b) poly (CPI-co-CPMI)

The data from Table 7 confirm the theory and are, in the same time, a proof that this polymerization mechanism leads to crosslinked three-dimensional networks with high degradation temperatures and fractional reaction orders.

Table 7. Kinetic parameters of the main thermal degradation stage for samples 3, 7

Sample	Weight loss (%)	on order n	Ea (kJ/mol)
3	38	2.52	285.56
7	30	2.51	345

CONCLUSIONS

- ⊕ Crosslinked functional beads containing alicyclic sequences were obtained.
- ⊕ The properties optimization referring the porosity, was performed by calculating and adjusting the solubility parameters used in synthesis (the diluents choice and their dosage).
- ⊕ In the present context, the porosity is the result of phase separation that occurs during the polymerization in the porogens presence.
- ⊕ A scheme for the mechanism of suspensions formation was proposed and the role of the factors that contribute to the uniform beads formation was highlighted.
- ⊕ The beads were morphologically characterized (AFM, SEM, TEM) in order to optimize the resulting structures and accumulate information about the role of the copolymers functionalization.
- ⊕ AFM analyses confirm formation mechanism of the crosslinked polymers, for the first time proposed by Kun and Kunin and developed by Dusek as: (1) the production and agglomeration of highly crosslinked gel microspheres, (2) the binding together with agglomerates and the matrix structure fixation.
- ⊕ The synthesized samples were tested by solvent retention and can form hydrophobic nanocontainers in polar solvents, and hydrophilic nanocontainers in apolar solvents.
- ⊕ Nanocapsules with polymeric structures, potentially useful as nanocontainers for high temperature, were obtained.

The objective of this stage was fully realized and some results were included into manuscripts submitted to publication.

Results dissemination

Original articles published in journals with impact factor

Influence of two structural phases of Fe₃O₄ and -Fe₂O₃ on the properties of polyimide/iron oxide composites
Nica, Simona-Luminita; Nica, Valentin; Grigoras, Vasile Cristian; et al.; *POLYMER INTERNATIONAL*
Volume: 64 Issue: 9 Pages: 1172-1181 Published: SEP 2015

Surface topography effect on fibroblasts population on epiclon-based polyimide films

Stoica, Iuliana; Barzic, Andreea Irina; Butnaru, Maria; et al.

JOURNAL OF ADHESION SCIENCE AND TECHNOLOGY Volume: 29 Issue: 20 Pages: 2190-2207
Published: OCT 18 2015

Polyimide precursor pattern induced by banded liquid crystal matrix: Effect of dianhydride moieties flexibility
Barzic, Andreea Irina; Hulubei, Camelia; Avadanei, Mihaela Iuliana; et al.

JOURNAL OF MATERIALS SCIENCE Volume: 50 Issue: 3 Pages: 1358-1369 Published: FEB 2015

Book chapters

Antibacterial Drugs: From Basic Concepts to Complex Therapeutic Mechanisms of Polymer Systems, in
“Antibacterial Agents”, ISBN 978-953-51-4274-4, Editura INTECH Andreea Irina Barzic and Silvia Ioan

Posters

Electrical resistivity under humidity conditions for plasma-treated and gold- sputtered polyimide films;
Simona- Luminita Nica, Camelia Hulubei, Iuliana Stoica, Emil Ghiocel Ioanid, Valentin Nica, Silvia Ioan ;
Zilele Academice Iesene, Progrese in stiinta compusilor organici si macromoleculari, Iași, 24 - 26 septembrie 2015;

Functionalized polymers for new applications; Luminita I. Buruiana, Raluca M. Albu, Silvia Ioan;

Conferinta Facultatii de Chimie-Zilele Universitatii, Iași, 29 oct. -30 octombrie 2015

Synthesis of a functional polymer as porous crosslinked beads containing alicyclic groups potentially useful as high temperature microcontainers; C.D. Vlad, I. Stoica, S. Nica, A. I. Barzic, C. Hulubei;

Conferinta Facultatii de Chimie-Zilele Universitatii, Iași, 29 oct. -30 octombrie 2015

PhD thesis , The thermodynamic study of some complex polymer systems under the influence of external factors,, supported by PhD student Simona Luminița Nica, Scientific adviser Dr. S. Ioan; “P. Poni” Institute of Macromolecular Chemistry, Iasi, 28. X. 2015

Director proiect,

