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## **EXPLORATORY RESEARCH PROJECT**

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

**- 2013 -**

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# BRIEF REPORT

concerning the results obtained by the project team between  
16 December 2012 – 15 December 2013

## Objective 3.

Synthesis and characterization of copolyimides (CPIs) containing soluble alicyclic diamine (CHDA, DCHM)

### *Associated Activities:*

3.1 Scientific documentation;

3.2 Purification of monomers and solvents;

3.3 Synthesis of soluble CPIs;

3.4 Confirmation of the CPIs structure by elemental analysis, IR and <sup>1</sup>H-NMR spectroscopy;

3.5 CPIs characterization: thermal stability (ATG, DSC), mechanical (DMA) and dielectric properties, CPIs films surface morphology (AFM, EDAX);

3.6 CPIs characterization in solution: flow behavior and viscoelastic properties.

### 3.1. *Scientific documentation*

Scientific premises:

*Copolymerization* is considered the most permissive and successful method for systematic effective changes in the polymers properties. Combination of rigid and flexible, aromatic and aliphatic monomers by copolymerization may be used to control the polymer mechanical and thermal properties, according to the specific requirements of high performance applications.

In general: \* alicyclic diamines- based CPIs are difficult to obtain due to their high basicity which causes salt formation; \* alicyclic dianhydride-based CPIs are more easily obtain, because some dianhydride such as that of bicyclo [2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic (BOCA) - in combination with aromatic diamines- has a reactivity higher than the pyromellitic anhydride (PMDA).

*Introduction of alicyclic units in the CPI structure:* \*aliphatic structures display a lower dielectric constant and higher transparencies which result from their lower molecular density and polarity and low probability of undergoing inter- or intra- molecular charge- transfer; incorporation of alicyclic units in a polymer backbone induces: solubility, thermal stability, negligible birefringence, low refractive index, lack of color.

*Introduction of fluorinated units in structure:* \*improves solubility, increases the polyimide films transparency, decreases dielectric constant (reduces interactions between CPI chains by steric hindrance).

### 3.2. *Purification of monomers and solvents*

CPIs obtained in this stage are polymers partially aliphatic, derived from pairs of alicyclic/aromatic dianhydride and diamine. Purification materials used for synthesis was achieved by various methods, presented in Table 1.

**Table 1. Materials used and purification methods**

Chemical Name	Provider	Abbrev.	Purification method
N-methyl-2-pirolidone	Aldrich	NMP	Vacuum distillation at 10 mmHg, dried on CaH <sub>2</sub> , stored on 4 Å molecular sieves
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
3,3',4,4'-Biphenyltetracarboxylic dianhydride	Aldrich	BPDA	Recrystallization from acetic anhydride, vacuum dried at 160 °C; p.t. = 301°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
4,4'-Methylenebis-(cyclohexylamine)	Aldrich	DCHM	Recrystallization from n-hexane ; p.t. = 45-46°C

### 3.3. Synthesis of soluble CPIs

Four partially soluble and transparent CPIs containing alicyclic dianhydride and diamines monomers (BOCA CHDA or DCHM) were synthesized. The copolymers were obtained by a polycondensation reaction of equimolar amounts of diamine and dianhydride, under anhydrous conditions using NMP as the solvent. The reaction occurs in two-stage, with the formation of polyamide acid (PAA) in the first stage and the thermal imidization of PAA to the CPI form, in the second stage.

The research strategy anticipates a synergism between the effects induced by:

\* *synthesis method*

- copolymerization of rigid and flexible monomers - that disrupts the symmetry and regularity of the polymer chain and allow to control thermal and mechanical properties of CPIs;

\* *structural changes of the backbone*

- incorporating of alicyclic monomers

\* BOCA – rigid and symmetrical molecule - that increases the solubility (by reducing the polymer-polymer interactions) and preserves the thermal stability (due to the multiple link from alicyclic structure);

\* CHDA- isomeric structure – destroys linearity of the chain, increases the interchain distance, lowers the energy necessary for rotation, lowers the T<sub>g</sub>, T softening and/or T<sub>m</sub> and increases solvent penetration in the polymer;

\* DCHM - large symmetrical molecule - induces flexibility;

- incorporating of Bulky groups / flexible links

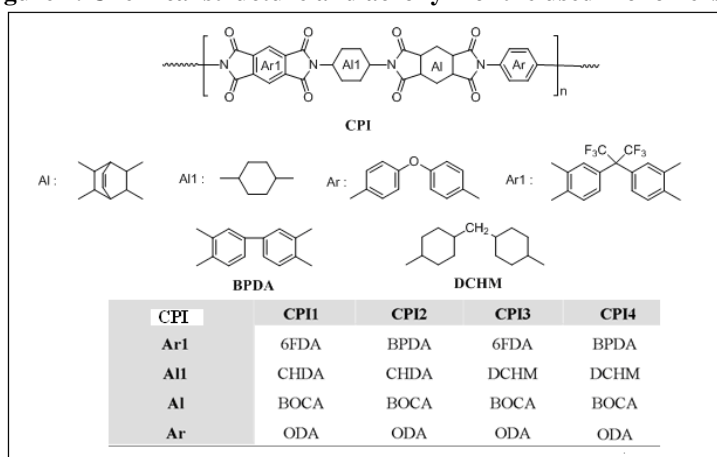
\* (-C (CF<sub>3</sub>)<sub>2</sub>-, -O-) - introduces “kinks” to the polymer chain which decrease the rigidity, inhibit the packing, reduce the intermolecular interactions, weaken the intensity of the yellow color, and increase the solubility.

### 3.4. Confirmation CPIs structure by elemental analysis, IR and <sup>1</sup>H-NMR.

IR spectra of CPI1-CPI4 show characteristic absorption peaks for: the imide structure to approx. 1774cm<sup>-1</sup> and 1710 cm<sup>-1</sup> (symmetric and asymmetric stretching vibration of C = O imide), approx. 1380 cm<sup>-1</sup> (stretching vibration of the imide ring C-N) and approx. 740 cm<sup>-1</sup> (imide ring deformation vibration); the aromatic structure at approx. 3053cm<sup>-1</sup> and 1501 cm<sup>-1</sup> (= CH in the benzene ring); aliphatic structure to approx. 2925-2854 cm<sup>-1</sup> (aliphatic groups of sequences DODCA and BOCA); ether bridges at about 1238 cm<sup>-1</sup> (- O-aromatic); 6F groups at about 1185 cm<sup>-1</sup> (in CPI1, CPI3);

\* **the absence of peaks at approx. 3350-3450 cm<sup>-1</sup> (broad band, associated with the NH group in the amide bond) and from 1650 to 1660 cm<sup>-1</sup> (associated with the C = O group in the amide bond) signifies the successful completion of the thermal imidization reaction of PAA to the PI structure.**

Figure 1. Chemical structure and acronym of the used monomers and the synthesized



<sup>1</sup>H NMR spectra of CPI1-CPI4 confirm:

- *aromatic protons* as the farthest signal towards standard signal from spectra;

- *vinyl protons* (from BOCA), the second farthest signal towards standard signal from spectra;

- *aliphatic protons* - methylene / methine - (from BOCA sequences, or DCHM CHDA) as specify chemical shifts  $\delta$  (ppm) in agreement with the proposed structures;

- *no amide/acid protons* - complete imidization;

The polymers obtained show: good solubility in dipolar aprotic solvents and the ability to form films. CPIs films were prepared by casting the polymer solution in NMP on the glass, followed by a special heating and drying. Film thickness obtained was about 40  $\mu\text{m}$ .

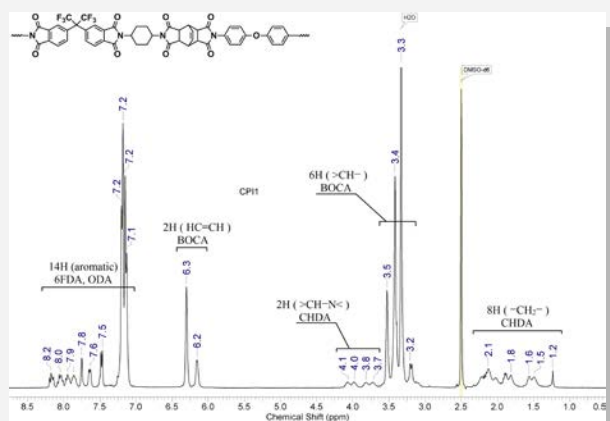


Figure 2.  $^1\text{H}$ -RMN spectrum of CPI1

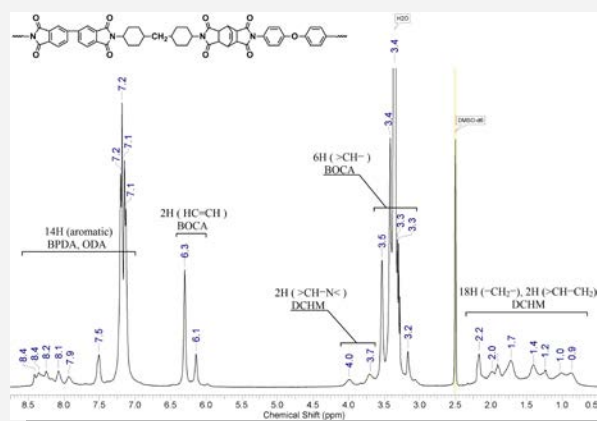


Figure 3.  $^1\text{H}$ -RMN spectrum of CPI4

### 3.5. CPIs characterization: thermal stability (ATG, DSC), mechanical (DMA) and dielectric properties, film surface morphology (AFM, EDAX)

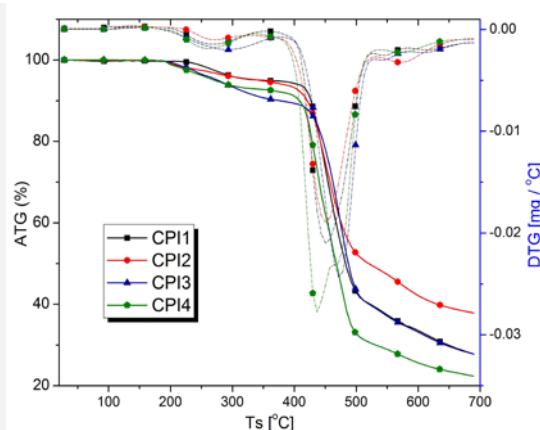


Figure 4. CPIs thermal behaviour

The thermal stability of the polymers was measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymers have a weight loss of 10% in the range of 375-430  $^{\circ}\text{C}$ , the first maximum decomposition temperature is in the range of 435-475  $^{\circ}\text{C}$ . That confirms that alicyclic structures is a balance factor in preserving the superior PI properties. The polymers show glass transition temperatures between 308  $\div$  326  $^{\circ}\text{C}$ , depending on their chemical structures. The results should be reported to the competition between the effects affecting glass transition: \* flexible connections

\* intra- and intermolecular interactions \* hydrogen bonds \* electrostatic and ionic forces, \* packing / macromolecular chain rigidity.

Dynamo-mechanical properties of CPIs films. Figure 5 shows the variation in  $E'$ ,  $E''$  and  $\tan \delta$  vs. temperature for CPI1 and CPI2 films.

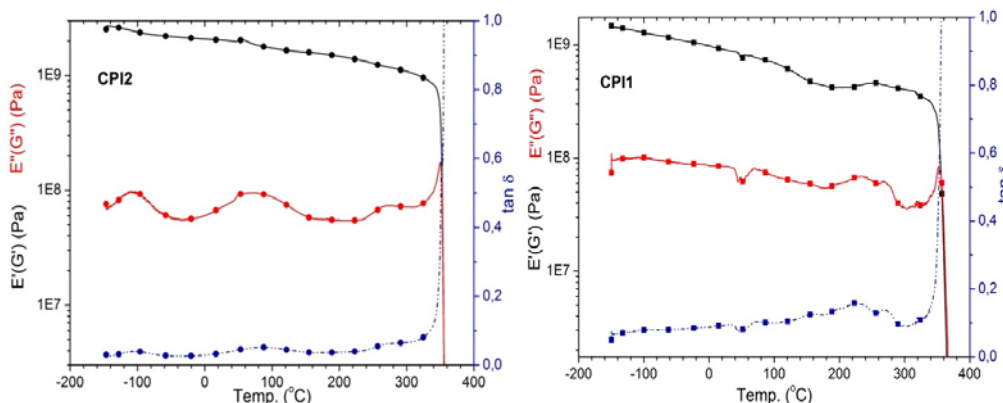


Figure 5. Variation of  $E'$ ,  $E''$  and  $\tan \delta$  with temperature for the films CPI1 and CPI2

From the representation of the loss factor  $\tan \delta = E'' / E'$  value on the entire temperature range for CPI2, at very low temperatures,  $\gamma$  and  $\beta$  relaxations (associated with low mobility of the macromolecular chain) can be observed. At -110  $^{\circ}\text{C}$   $\gamma$  relaxation, associated with the release of water molecules retained within CPIs

film appears, and at approx.  $-100\text{ }^{\circ}\text{C}$  another  $\gamma$  relaxation, possibly due to the oscillation of the phenoxy group from the CPI structure appears.

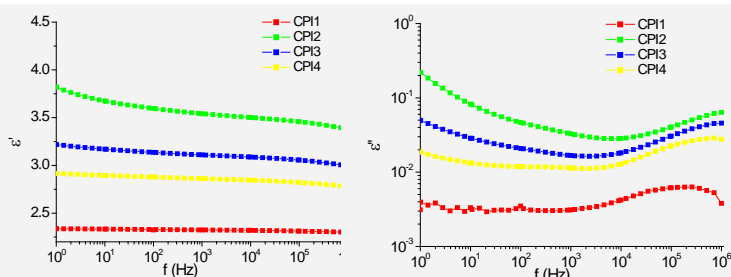
At temperatures higher than room temperature the  $\beta$  relaxations occur associated with the mobility of chain segment and their rotation around the flexible links. At  $+80\text{ }^{\circ}\text{C}$  there is a first  $\beta$  relaxation attributed to the release of polar molecules. At higher temperatures, close to the glass transition temperature, there is a second relaxation  $\beta$ , of lower intensity, possibly due to the oscillation of the bicyclo group from BOCA dianhydride structure. At temperatures above  $300\text{ }^{\circ}\text{C}$ ,  $E'$  and  $E''$  sharply decrease while  $\tan\delta$  increases starting with  $344\text{ }^{\circ}\text{C}$ , temperature corresponding to the transition temperature glassy.

A similar behavior was observed for CPI1. However, due to higher volume of this macromolecular chain and the weaker polymer packing properties induced by the presence of bridge groups 6F, the slope of the elastic modulus  $E'$  is steeper, the value of this energy is lower. From the representation of the  $\tan\delta$  versus temperature, it is observed that, the  $\gamma$  transition around temperature of  $-100\text{ }^{\circ}\text{C}$  is very weak, which means that the amount of water held in the film is lower. The  $\gamma$  Relaxation at  $-100\text{ }^{\circ}\text{C}$  can be attributed exclusively to the motion of the phenoxy groups derived from the aromatic diamine structure.

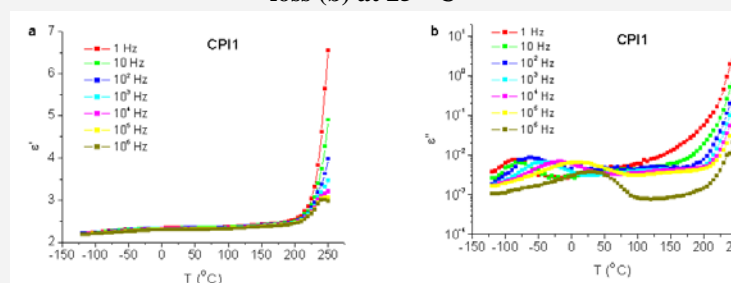
Near the temperature of  $+80\text{ }^{\circ}\text{C}$ , similar to the CPI2, a first mild  $\beta$  relaxation, occurs. Other two  $\beta$ -type relaxations there are at  $155\text{ }^{\circ}\text{C}$  and  $225\text{ }^{\circ}\text{C}$  respectively, that can be attributed to the oscillation and rotation movements induced by the groups 6F; the relaxation of  $280\text{ }^{\circ}\text{C}$  can be associated with the oscillation movement of the structure originating from bicyclo in BOCA. As in the case CPI2,  $\alpha$  relaxation occurs when the temperature increases at  $340\text{ }^{\circ}\text{C}$ ; at this temperature the polymer softens and pass in viscoelastic state.

**Measurements of complex dielectric permittivity  $\epsilon^* = \epsilon' + i\epsilon''$**  where  $\epsilon'$  is the permittivity or the dielectric constant and the imaginary part  $\epsilon''$  is the dielectric loss, were conducted on extensive areas of temperature ( $-120 \div 250\text{ }^{\circ}\text{C}$ ) and frequency ( $1\text{ Hz} \div 10^6\text{ Hz}$ ), on the relatively thin film of about  $40\text{ }\mu\text{m}$ .

**The dielectric constant values at room temperature** for all CPIs are less than 4. These constants are comparable for the polymer CPI2 and are smaller for the other polymers (the dielectric constant value of the commercial PI Kapton,  $\epsilon'_{\text{Kapton}} = 2.69\text{-}2.90$ ). This result is due to the presence of groups with low polarizability (alicyclic and 6F).



**Figure 6. Variation of frequency permittivity (a) and dielectric loss (b) at  $25\text{ }^{\circ}\text{C}$**



**Figure 7. Variation of permittivity and dielectric loss at some frequencies  $T^{\circ}$  for CPI1**

Although fluorine is the most electronegative element, the presence of symmetric trifluoromethyl groups leads to the annulment of the total dipole moment of the group.

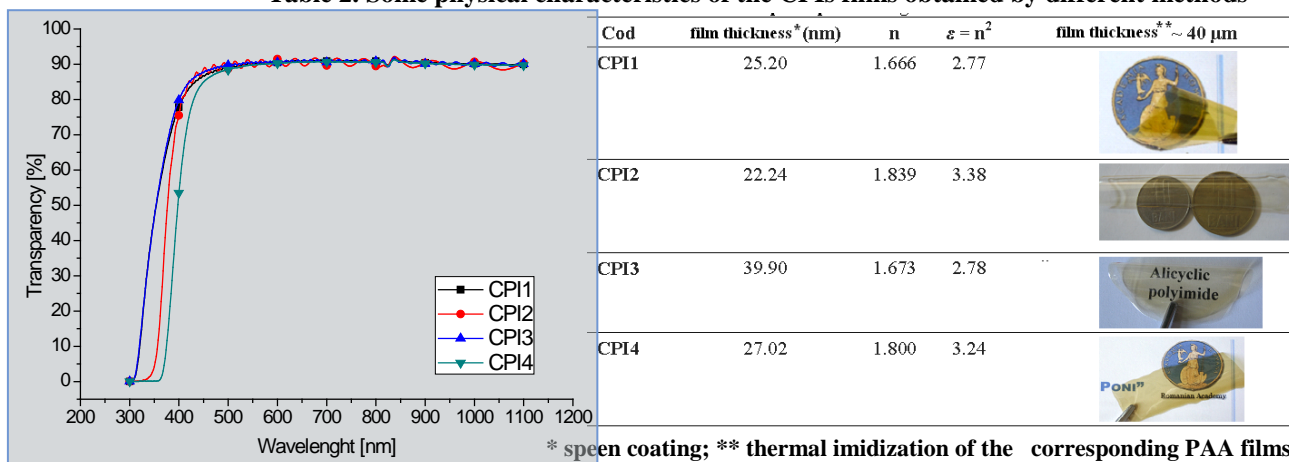
In addition to alicyclic groups, 6F bridge determines an increased free volume and induces a dilution effect of the polarizable groups number of per unit volume.

With frequency increasing there is a slight decrease in permittivity due to the dipolar polarization, molecular dipoles having enough time to guide the direction of the applied electric field. Dielectric loss values are lower than  $10^{-1}$  at  $25\text{ }^{\circ}\text{C}$ , with the exception CPI2, and remain low up to about  $150\text{ }^{\circ}\text{C}$  for CPI2 and CPI3 and  $200\text{ }^{\circ}\text{C}$  for CPI1 & CPI4 respectively.

***This property allows the use CPI1-CPI4 as very good dielectrics to relatively high temperature.***

**CPIs transparency.** The synthesized polymers have a very good transparency with a transmittance greater than 85% at 400 nm. The wavelength limit at which the transmittance is less than 1% is 310 nm for CPI1, 338 nm for CPI2, 310 nm for CPI3 and 364 nm for CPI4.

**Table 2. Some physical characteristics of the CPIs films obtained by different methods\*\* \*\***

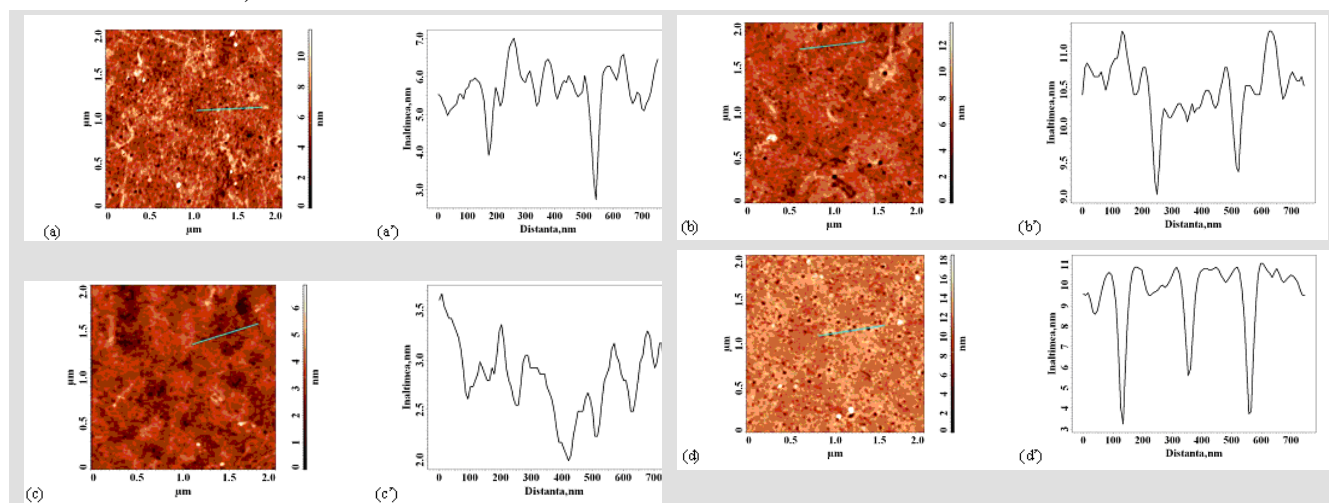


**Figure 8. CPIs transparency**

**CPIs films surface morphology** was investigated by atomic force microscopy (AFM). Investigations have shown that CPI1-CPI4 films have a good quality and are very smooth and uniform, with the mean square roughness values below 1 nm. On their surface can be seen the existence of nanometric pores, whose number varies from one sample to another, depending on the CPI chemical structure. (Table 3).

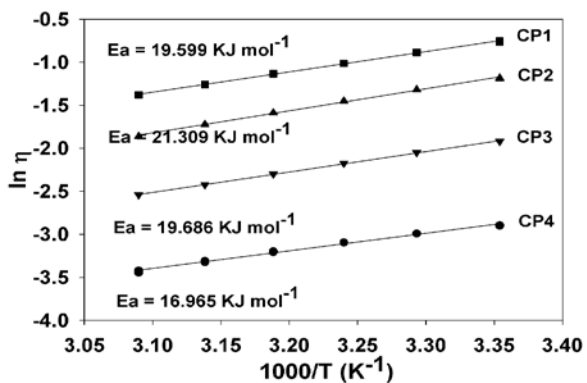
Table 4. CPIs nanopores characteristics from AFM images				Table 3. CPIs roughness parameters from AFM images			
Sample	D medium (nm)	Average depth (nm)	Pores density (pores/ $\mu\text{m}$ )	Sample	D medium (nm)	Average depth (nm)	Pores density (pores/ $\mu\text{m}$ )
CPI1	30 $\pm$ 8	6 $\pm$ 0.6	14	CPI1	30 $\pm$ 8	6 $\pm$ 0.6	14
CPI2	47 $\pm$ 8	10 $\pm$ 2	33	CPI2	47 $\pm$ 8	10 $\pm$ 2	33
CPI3	30 $\pm$ 6	5 $\pm$ 0.6	20	CPI3	30 $\pm$ 6	5 $\pm$ 0.6	20
CPI4	30 $\pm$ 16	12 $\pm$ 3	63	CPI4	30 $\pm$ 16	12 $\pm$ 3	63

By analyzing the topographic images and the corresponding height profile for the CPIs samples and tacking into account that BOCA-ODA is a common segment for all CPIs, was found that samples containing in their composition BPDA have a greater ability to form pores prominently. It is possible that the dianhydride structure to induce rigidity to the CPIs backbone, resulting in a conformation capable of generating intrinsic porosity (see Table 3 and Table 4).



**Figure 8. AFM topographic images and the corresponding cross-section profiles: CPI1 (a, a'), CPI2 (b, b'), CPI3 (c, c') și CPI4 (d, d')**

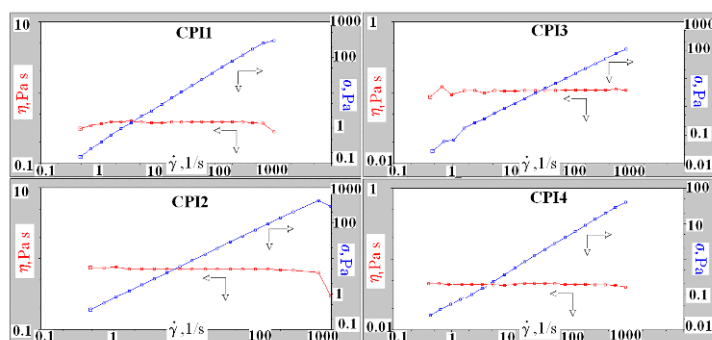
### 3.6. CPIs characterization in solution: flow behavior and viscoelastic properties



**Figure 9.** Arrhenius representation to obtain the flow activation energy,  $E_a$ :  $(\ln \eta = \ln \eta_0 + \frac{E_a}{RT})$

The rheological study refers to the CPI1 ÷ CPI4 viscoelastic properties changing under the influence of some structural features generated by the different chemical aliphatic / aromatic segments in the backbone, with various flexibility and specific hydrophobicity degrees.

It has been found that these copolymers exhibit Newtonian flow, the changes of the dynamic viscosities in N-methyl-2-pyrrolidone (NMP) depending on the rigidity of the components and the interpenetration degree of the macromolecular chains (Figure 9).

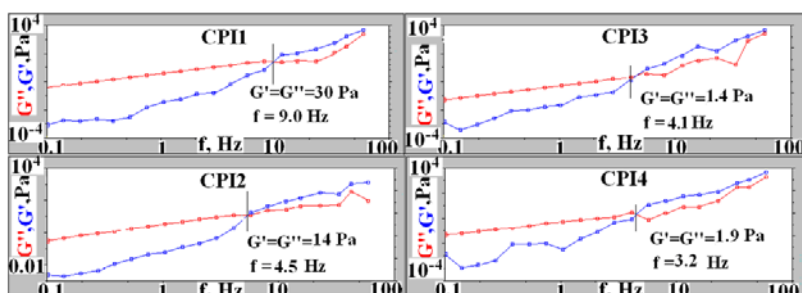


**Figure 10.** Double logarithmic graphs for CPI1 - CP4 dynamic viscosity in NMP ( $\eta$ , left ordinate), shear stress ( $\sigma$ , right ordinate) and shear rate ( $\dot{\gamma}$ ).

Because the copolymers have in common the segments BOCA-ODA, the conformational changes in solution are mainly due to the aromatic dianhydride sequences (6FDA - more flexible than BPDA) and the less the corresponding

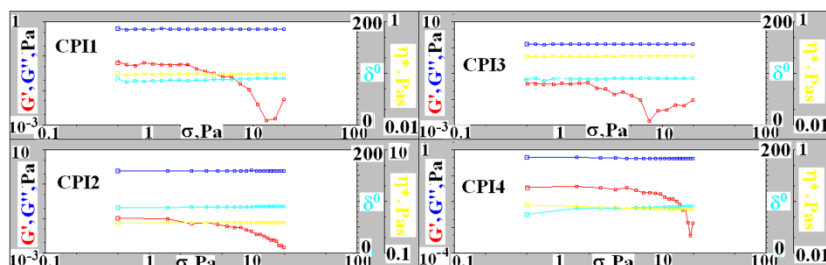
cycloaliphatic diamines.

In particular, the higher rigidities of the dianhydrides and mentioned diamines (BPDA, respectively CHDA) induce geometric constraints in the macromolecular chains and determine thus a greater CPIs rigidity reflected in their properties. The dynamic viscosities (0.70; 0.38; 0.10; respectively 0.04 Pa.s) (Figure 10) and flow activation energies (21.31; 19.60; 19.69, respectively, 16.96) satisfy the global CPIs flexibility trend. On the other hand, the dependence of the viscous moduli,  $G''$ , and elastic  $G'$ , on frequency follow a power law where exponents are approximately equal to 1 and 2 respectively (Figure 11).



**Figure 11.** Double logarithmic plots of the viscous modulus ( $G''$ ) and elastic ( $G'$ ) versus frequency of oscillation for CPI1-CP4 in NMP at 25 ° C (concentration of 15 g / dl).

For these studies we chose a viscoelastic shear stress of 6Pa, according to amplitude tests from Figure 12.



**Figure 12.** The double graph of the logarithmic viscous modulus,  $G''$ , and elastic,  $G'$ , depending on shear stress, for CPI1 - CP4 in NMP at 25 ° C (concentration of 15 g/dl)

The transition from the viscous at elastic field, defined by  $G' = G''$ , occurs at lower frequency with as the copolymer rigidity increases. For all studied CPIs, the rheological properties are influenced by the characteristics of hydrophobicity. Low polarization correlated with a high stiffness is due to dipole orientation and charge carriers responsible of electron-donating interactions.

*Depending on the structures of these CPIs, the factors which lead to changes in the interactions involved in their rheology can be optimized to obtain the required properties for different application domains.*

All objectives were fully realized in this stage and some results were included into manuscripts submitted to publication.

### Results dissemination

- 4 papers were published in journals indexed by web of knowledge.
- The team members participated at 7 scientific events with 3 oral presentations and 4 posters.

### Published papers in journals with impact factor

**1. Surface Properties and Blood Compatibility of Some Aliphatic/Aromatic Polyimide Blends**, Simona-Luminita Nica, Camelia Hulubei, Iuliana Stoica, Ghiocel Emil Ioanid, Silvia Ioan, *Polym. Eng. Sci.*, **53 (2)**, 263–272, **Feb. 2013**, (Articol aparut online: 17 Iulie 2012).

**2. An insight on the effect of rubbing textile fiber on morphology of some semi-alicyclic polyimides for liquid crystal orientation**, Andreea Irina Barzic, Iuliana Stoica, Dumitru Popovici, Stelian Vlad, Vasile Cozan, Camelia Hulubei, *Polym. Bull.*, **70 (5)**, 1553-1574, **May 2013**, (Articol aparut online: 26 Septembrie 2012).

**3. Origin of dielectric response and conductivity of some alicyclic polyimides**, Silvia Ioan, Camelia Hulubei, Dumitru Popovici, Valentina Elena Musteata, *Polym Eng. Sci.*, **53 (7)**, 1430 - 1447, **July 2013**, [DOI 10.1002/pen.23409](https://doi.org/10.1002/pen.23409) (Articol aparut online: 28 Noiembrie 2012).

**4. Origin of rheological behavior and surface/interfacial properties of some semi-alicyclic polyimides for biomedical applications**, Silvia Ioan, Anca Filimon, Camelia Hulubei, Iuliana Stoica, Simona Dunca, *Polym. Bull.*, **70 (10)**, 2873 - 2893, **Oct. 2013**.

### Scientific events

#### Conferences

**Crosslinkable aromatic/alicyclic copolyimides**, Cristina Vlad, Iuliana Stoica, Dumitru Popovici, Cristina Zgardan, Camelia Hulubei, *11th Conference on Colloid and Surface Chemistry*, Iasi, Romania, **9-11 Mai 2013**, p. 3.

#### Communications

**New processable polyimides containing alicyclic units for advanced technology**, Dumitru Popovici, Camelia Hulubei, Silvia Ioan, Maria Bruma, *Interacademic Romania – Poland Exchange*, Zabrze, Poland, **30 Iulie 2013**.

**Synergistic effects of some semi-alicyclic polyimide on the work of liquid adhesion/cohesion**, Silvia Ioan, Anca Filimon, Camelia Hulubei, Emil Ghiocel Ioanid, *18th Romanian International Conference on Chemistry and Chemical Engineering, RICCE XVIII*, Sinaia, Romania, **4-7 Septembrie 2013**, p. 13.

#### Posters

**New partially aliphatic copolyimides films modified by plasma treatment for high performance applications**, Dumitru Popovici, Irina Andreea Barzic, Maria Butnaru, Iuliana Stoica, Camelia Hulubei, *5th European Exhibition of Creativity and Innovation - EUROINVENT*, Iasi, Romania, **9-11 Mai 2013**, p. 209 - Silver Medal.

**Influence of casting solution properties on the morphological characteristics of some alicyclic polyimides films**, Silvia Ioan, Anca Filimon, Camelia Hulubei, Iulia Stoica, *International Conference of Physical Chemistry, RomPhysChem 15*, Bucuresti, Romania, **11-13 Sept. 2013**, p. 17.

**Physical characterization of some partial aliphatic copolyimides based films**, Camelia Hulubei, Silvia Ioan, Dumitru Popovici, Jan Wieszka, Iuliana Stoica, Valentina Elena Musteata, Gabriela Lisa, *A XXIV-a Sesiune de comunicari stiintifice a Institutului de Chimie Macromoleculara „Petru Poni” Iasi “PROGRESE IN STIINTA COMPUSILOR ORGANICI SI MACROMOLECULARI”*, Iasi, Romania, **3-5 Octombrie 2013**, p. 13.

**Originea configurationala a modificarilor viscoelastice ale unor copoliimide partial aliciclice**, Silvia Ioan, Anca Filimon, Camelia Hulubei, *A XXIV-a Sesiune de comunicari stiintifice a Institutului de Chimie Macromoleculara „Petru Poni” Iasi “PROGRESE IN STIINTA COMPUSILOR ORGANICI SI MACROMOLECULARI”*, Iasi, Romania, **3-5 Octombrie 2013**, p. 16.

Director proiect,

