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

- 2012 -

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BRIEF REPORT

concerning the results obtained by the project team between
16 December 2011 – 15 December 2012

Objective 1. Synthesis and characterization of homopolyimide (hPI) containing alicyclic dianhydride (DOCDA and BOCA) to obtain high performance alignment layers (Als).

Associated Activities:

1.5 hPI characterization in solution: flow behavior and viscoelastic properties.

1.6 hPI solid state characterization: thermal stability (ATG, DSC), mechanical (DMA) and dielectric properties, refractive index evaluation, transparency and absorption limits, hPI films surface morphology (SEM, AFM) investigation.

Objective 2. Change of the hPI film surface morphology by reorganizing topography to obtain high performance alignment layers for liquid crystal (AlCLs)

Associated Activities:

2.1. Changing of hPI films morphology by rubbing with different textiles.

2.2. Changing of hPI films morphology by printing liquid crystalline matrix.

2.3. The effect of structural organization and intrinsic architecture on the molecular orientation of LC molecules deposited on the hPI surface.

2.4. The influence of the nature textile fiber on the CL degree alignment.

2.5. Effect of induced molecular organization of polyimide film matrix CL alignment on the properties.

2.6. Testing of liquid crystal films deposited on HPI for applications such as alignment layers.

Objective 1. Synthesis and characterization of polyimide (PI) containing alicyclic dianhydride (DOCDA and BOCA) to obtain high performance alignment layers.

1.5. hPI characterization in solution: flow behavior and viscoelastic properties.

The results show structural processes that influence the dynamic viscosity and viscoelasticity of different flexible partially aliphatic hPI, poly (DOCDA-ODA), poly (p-BAPS DOCDA), poly (BOCA-ODA) and poly (p-BAPS- BOCA) .

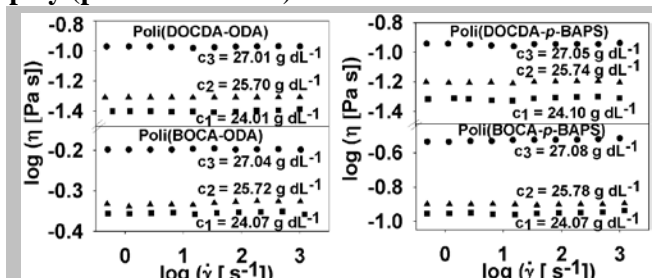


Figure 1. The dynamic viscosity according to the shear rate for PI solutions in NMP at 25 °C

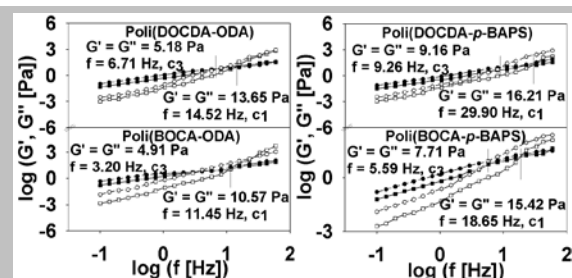


Figure 2. Viscous and elastic moduli frequency for PI solutions in NMP at 25 °C

Investigations carried out in solution, using as solvent 1-methyl-2-pyrrolidone (NMP). Figures 1 and 2 present: * a Newtonian behavior of the dynamic viscosity depending on the shear rate;

* higher dynamic viscosities values for hPI containing BOCA dianhydride, than the corresponding hPI containing DOCDA dianhydride;

* values of the dynamic viscosities less than both hPI-containing the diamine p-BAPS compared to those of containing ODA, possible due to the steric hindrance caused by -SO₂ groups in the diamine p-BAPS and those induced by the no coplanar bicycle from BOCA dianhydride, respectively; as result, there is an increasing of the free volume (by decreasing the polymer chain packing and diluted the number of polarized groups per unit volume), ultimately increasing the solubility;

* lower values for the viscoelastic moduli and higher values of the oscillatory frequency for the transition from the elastic to viscous field are obtained when the hPI flexibility containing the same dianhydride increases, by the presence in the chemical structure of p-BAPS diamine;

* lower values of oscillatory frequency corresponding of the transition from viscous to elastic at higher PI concentrations solutions are obtained;

* the storage and loss moduli follow a power law function of frequency where the exponents of about 2 and 1, respectively, are characteristic for viscoelastic fluids. In general, it was found that the similarity between the structures of the PI chain having a common monomer (diamine or dianhydride) significantly influences the rheological properties.

1.6 hPI solid state characterization: thermal stability (ATG, DSC), mechanical (DMA) and dielectric properties, refractive index evaluation, transparency and absorption limits, hPI films surface morphology investigation (SEM, AFM).

From the results obtained it appears that the synthesized hPI: * are soluble in the aprotic dipolar solvent (NMP, DMAc, DMF) and partially soluble or insoluble in the other (THF, CHCl₃, toluene, ethanol, etc.);

* are highly thermal stable (ATG, DSC) without significant loss of mass to 430 ° C (Table 1); * have dielectric constants in the range of 2.73 ÷ 3.33.

Table 1. Some physical and chemical characteristics of synthesized hPIs

Sample	Cod	M ₀	M _n	P	T _g (°C)	IDT (°C)	T ₁₀ (°C)	T _d (°C)	Y _c (%)
poly(DOCDA-ODA)	PI1	428,4	20998	1,55	238	429	439	489	27,24
poly(DOCDA-pBAPS)	PI2	660,7	29419	1,40	191	433	465	496	44,70
poly(DOCDA-6FADE)	PI3	746,6	21481	1,61	229	434	458	502	22,23
poly(BOCA-ODA)	PI4	412,4	53104	1,64	390	428	445	460	22,12
poly(BOCA-pBAPS)	PI5	644,7	43664	1,62	320	440	471	483	43,23
poly(BOCA-6FADE)	PI6	730,6	43011	1,72	–	–	–	–	–

M₀- molecular weight of US; M_n- Number average molecular weight; P- polydispersity T_g-temp. glass transition; IDT-temp. onset of thermal decomposition; T₁₀-temp. corresponding to 10% of weight loss; T_d-temp. max. Decomposition of DTG curve; Y_c-carbonaceous residue at 700 ° C

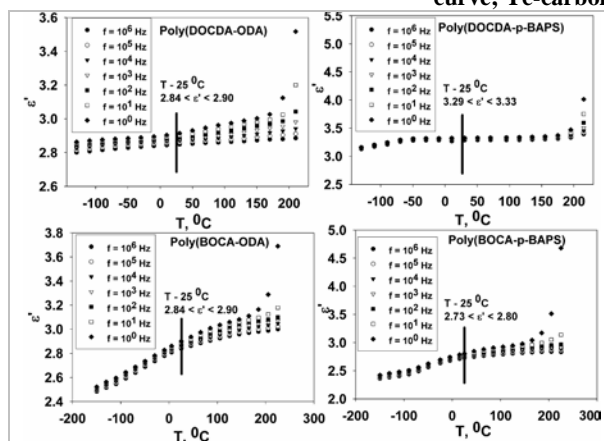


Figure 3. Dielectric constant versus temperature at different frequencies: poly(DOCDA-ODA), poly(DOCDA-p-BAPS), poly(BOCA-ODA), poly(BOCA-p-BAPS)

Detailed studies of hPI show:

* *dielectric constant* decreases with increasing frequency - Figure 3- being influenced by the total polarizability of the chain (dipole orientation and preventing of the electronic conjugation);

* γ and β relaxations arise from the increased mobility of the polymer chain at increasing temperature, resulting from different parameters (dielectric spectroscopy measurements and DMA);

* γ *relaxation* corresponds isolated movements, necooperative - activation energy is mainly an enthalpic process; a lower value results for the polymers containing p BAPS diamine (due to steric hindrance effects induced by SO₂ group);

* β *relaxation* occurs due to the dipole orientation and increase for the PI containing BOCA dianhydride segments;

* *the structural parameters of the polymer chain* results in a different modification of the conductivity in AC with the temperature and frequency;

* *the value of the activation energy of the electric conductivity* is the result of electron transfer mechanism caused by temperature.

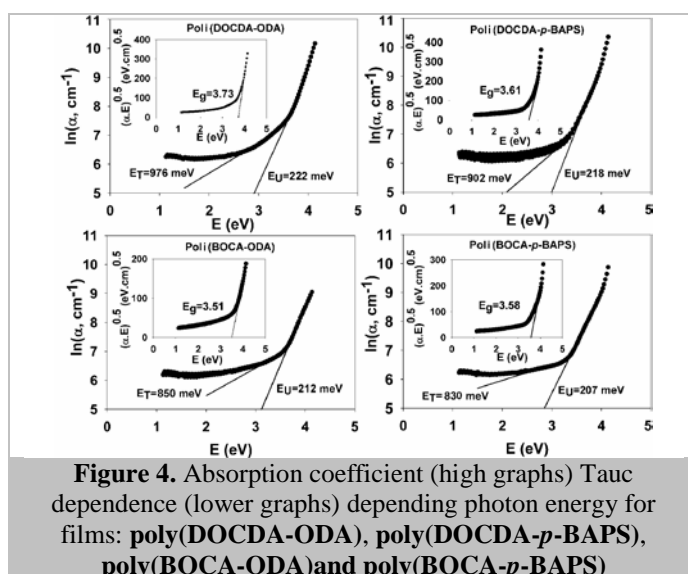
Transmission spectra of **poly (DOCDA-ODA)**, **poly (p-BAPS DOCDA)**, **poly (BOCA-ODA)** and the **poly (p-BAPS BOCA)** allowed evaluation of the energy band gap (3.73, 3.61; 3.51; 3.58 meV) and Urbach energies characteristic to the absorption limit (222, 218, 212, 207 meV) and Tauc band gap energy exponential tail (976, 902, 850, 830 meV).

Transmission spectra obtained from the ultraviolet range at about 450 nm, showing a transparency around 90% for all PI studied (Figure 4). It is found that:

* values for these energies, E_G, E_U și E_T correspond to conduction through a jump-type mechanism so that model based on the representation of the band gap (specific for semiconductor materials) may be appropriate to explain the electrical conductivity;

* values for Urbach and Tauc energies, as those for the band gap, correspond to transparent materials;

* the differences between optical and electrical band gap energy can be explained if we assume that the optical energy band gap of a system is dependent on the photon energy intensity of the photoluminescence spectrum and that the band gap energy is a result of the relaxation processes that occur by modification temperature.



The obtained results recommend the investigated hPI for advanced applications in microelectronics.

Objective 2. Change of the hPI film surface morphology by reorganizing topography to obtain high performance alignment layers for liquid crystal (AICLs).

Dielectric and optical properties of the hPI films obtained in this project, recommended that displays as AICLs to obtain type LCD (liquid crystal display). We propose two techniques for processing their morphology: * *rubbing with different textiles* and * *printing matrix liquid crystal*.

2.1. Changing of hPI films morphology by rubbing with different textiles.

Modeling the PI films surface by rubbing with textiles is a the most used method in achieving LCD displays. The CL mechanism guidance on rubbed surfaces is discussed in the literature from different perspectives: * steric interactions between nanogrooves (generated by the film surface deformation after rubbing) and CL; * van der Waals interactions between CL and PI macromolecules anisotropic oriented by rubbing; * influences induced by the chemical structure, PI chain conformation at surface film, rubbing parameters (the friction force and density of fibers in the used textiles), the residual solvent in film and the hydrophobic characteristics of rubbed film surface. There are no reports, however, on the effects of the various textile materials in the process of rubbing. For this reason, two hPI films of (PI-4 & PI-5) obtained from cycloaliphatic dianhydride of bicyclo [2.2.2.] oct-7-ene-2,3,5,6-tetracarboxylic acid (BOCA) and the diamines 4,4-oxidianilina (ODA) and 4-(4-{[4-(4-aminophenoxy)-phenyl]sulfonyl}phenoxy)aniline - (p-BAPS) respectively, were rubbed a minute with natural velvet, VC or synthetic, VCD, mounted on a cylinder with a diameter of 12 mm, with a constant contact pressure and a rotational speed of 200 rpm.

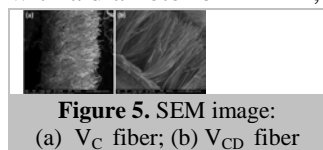


Figure 5 shows a scanning electron microscopy image (SEM) of the layout, shape and dimensions of velvet fibers used: (a) VC average fiber -length of 950 micrometres, thickness of 15 μm ; (b) VCD- fiber length of 1.5 mm and a thickness of 25 μm . Analyses of atomic force microscopy (AFM) before and after rubbing were made by Semi technique at room temperature. Velvets used

to generate the increase of the film surface micro-roughness. Figure 6 shows the surface morphology of films PI and their profile (surface scan: 10x10 μm^2). Analyses profile - Fig.6 b, d - reveals the presence of nanometric grains which creates a mean roughness of 4.5 nm for poly (BOCA-ODA) and 1.5 nm for poly (BOCA-pBAPS). The morphology of the films processed (Figures 7, 8) shows that the granules initially observed disappear, forming microgrooves parallel to the direction of friction, essential to align LC molecules. Depending on the structure of the textile used, results different topography type grooves, with different sizes, similar to other alignment layers based on PIs.

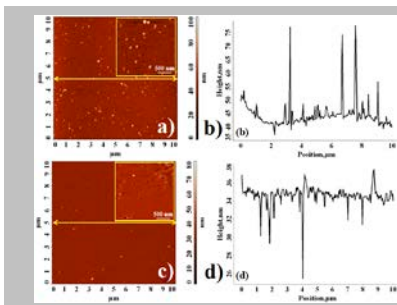


Figure 6. The morphology and surface profile of PI films: poly(BOCA-ODA) (a, b); poly(BOCA-pBAPS) (c, d)

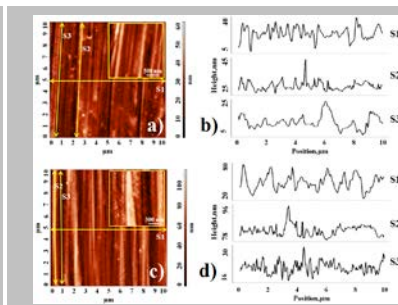


Figure 7. AFM images and surface profiles after various fracture lines, for poly(BOCA-ODA) rubbed with (a) V_C ; (b) V_{CD}

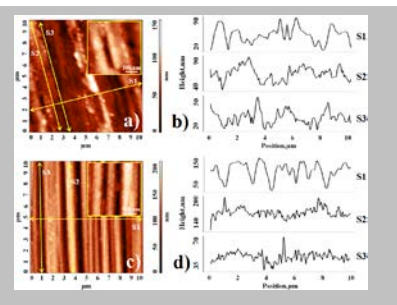


Figure 8. AFM images and surface profiles after various fracture lines, for poly(BOCA-pBAPS) rubbed with (a) V_C ; (b) V_{CD}

2.2. Changing of hPI films morphology by printing liquid crystalline matrix. The project examines *the possibilities to obtain new alignment layers by mixing the PI with a CL as an alternative to low thermal stability and dimensional ALs*, thus achieving a balance between the properties of the individual components. The surface anisotropy of optical and mechanical properties of films from the systems polymer / anisotropic phase and their possible use as ALCLs makes them important for new applications.

Hydroxypropyl cellulose (HPC) in solution, depending on the concentration and the nature of solvent, presents LC optical properties and an helical arrangement.

The possibility of inducing the ordering existing in the LC to the other component in the system is un studied direction for a range of mixtures polymer/HPC.

The project proposes a new method for preparing mixed alignment layers, using as a LC matrix, HPC in lyotropic phase. To efficiently induce the characteristic bands of HPC (LC) is performed mixtures with polyimide precursor (PAA) in order to achieve specific interactions (hydrogen bonds) with a role in the morphology stabilization. Two polymers derived from the same diamine, 4,4'-(hexafluoroisopropylidene) bis(p-phenyleneoxy) dianiline (6FADE) and different alicyclic dianhydrides DOCD A and BOCA respectively, are used. The steps of preparing the mixed ALCLs are the following:

- * obtaining of HPC in lyotropic phase {solution 65% grav. HPC in N, N-dimethylacetamide (DMAc)};
- * obtaining of solutions PAA_{DOCD A-6FADE} and PAA_{BOCA-6FADE}, concentration 50% grav. in DMAc;
- * realization of lyotropic phase mixtures (HPC) / PAA solution in mixing ratios of: 25/75, 50/50, 75/25 grav./grav.;
- * the obtaining of films from the resulting mixtures.

The induced morphological changes in the obtained systems were analyzed by polarized light microscopy (PLM) and AFM. HPC films shows a chiral nematic structure increasingly more pronounced towards concentration of 65% grav. anisotropic phase. In a shear field, chiral nematic arrangement changes in texture organized, consisting of alternating light and dark lines perpendicular to the shear direction. The morphology of these systems is influenced by the ratio in which there are the two components PAA / HPC (Figure 9). PLM studies reveal the presence of droplet sorting (associated with LC domains) alternating with black regions (associated with PAA domains). At concentrations of component LC > 50% grav. the droplets disappear, resulting in a mosaic-like morphology [alternation of regions birefringent (anisotropic phase) and black regions (isotropic phase)].



Figure 9. Images of polarized light microscopy of HPC and of the mixtures in various reports with the two PI precursors

Transferring the bands structure of the CL to PAA component was investigated by AFM.

For the HPC films in lyotropic phase can be distinguished at right angles to the direction of shear, the primary set high band, and a smooth texture, characterized by a second periodic structure, useful for achieving ordered polymer films with a LC template (Fig. 6).

By mixing LC(HPC) with isotropic component (PAA), surface topography changes (Fig. 6, 7), both systems PAA / HPC showing strip texture even for a high content of PAA

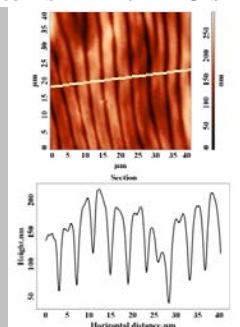


Figure 10. AFM image of film HPC solution 65% grav. in DMAc and the perpendicular profile of to the primary lanes set

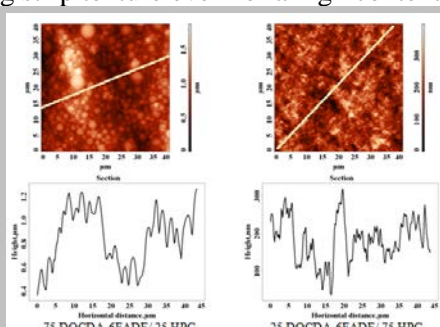


Figure 11. AFM images of the system PAA (DOCDATA-6FADE)/HPC in the mixing reports of: 75/25 și 25/75 grav./grav.

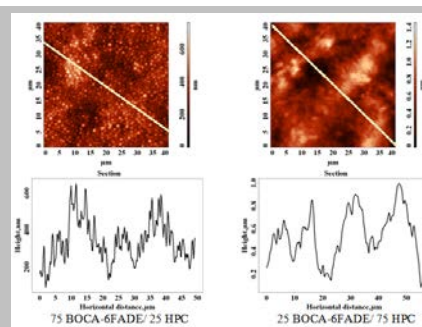


Figure 12. AFM images of the system PAA(BOCA-6FADE)/HPC in the mixing reports of: 75/25 și 25/75 grav./grav.

The periodic fluctuation of the LC director around the shear direction can be adjusted by the isotropic component, bands size varying depending on the amount of added PAA (ex.: from 20 μm to 75/25 grav./grav. to 5 mm for 75/25 grav./grav. -system Fig. 11 and from 14 μm for 75/25 grav./grav. to 10 micrometres for 75/25 grav./grav. respectively - system Fig. 12.). In the both cases, the increase in HPC content decreases bands thickness and the disappearance of the grain structure, in agreement with the PLM results. *The proposed method is simple and cheap and leads to adjustable mixed alignment layer morphology depending on system composition.*

2.3. The effect of structural organization and intrinsic architecture on the molecular orientation of LC molecules deposited on the hPI surface. 2.4. The influence of the textile fiber nature on the LC alignment degree. The objectives 2.3. and 2.4. are discussed simultaneously because the LC alignment properties depend on: * PI chemical structure, *conformation and degree of the PI packing, *mechanical and surface properties *nature of textile fibers involved in rubbing. The size and properties of textile fibers were essential in the design of resulted surfaces. For both studied samples, **poly (BOCA-ODA)** and **poly (BOCA-pBAPS)**, natural velvet V_C , with short fibers and low flexibility, generates deeper microgrooves (with valley and hill conformation oriented in the rubbed direction) and with a better regularity compared to those obtained with *synthetic velvet*, V_{CD} .

Table 2. Analysis of roughness and grooves characteristics obtained for the investigated PI films

Sample	Roughness		groove characteristics			
	S_q (nm)	S_{ent}	Main groove		Side groove	
			width (nm)	depth (nm)	width (nm)	depth (nm)
poly(BOCA-ODA)	4.5	7.6	-	-	-	-
poly(BOCA-ODA)/ V_{CD}	6.9	8.8	433.5 \pm 168.9	25.2 \pm 1.1	159.3 \pm 39.5	16.5 \pm 3.5
poly(BOCA-ODA)/ V_C	16.6	10.1	580.4 \pm 95.60	63.5 \pm 7.3	186.6 \pm 12.2	24.6 \pm 2.3
poly(BOCA-pBAPS)	1.5	5.7	-	-	-	-
poly(BOCA-pBAPS)/ V_{CD}	19.7	10.3	695.7 \pm 178.3	36.3 \pm 4.1	275.0 \pm 66.5	39.3 \pm 1.4
poly(BOCA-pBAPS)/ V_C	39.9	11.2	916.3 \pm 81.8	119.0 \pm 14.7	326.3 \pm 39.8	82.6 \pm 14.4

S_q : mean square roughness; S_{ent} : Entropy of surface - calculated by the software device

A statistical analysis of the micro-grooved morphology, made on multiple sections along them, enabled the measurement of mean square roughness (S_q) for each sample (Table 2). For **poly (BOCA-ODA)** the mean square roughness indicates a more uniform surface of microgrooves obtained by rubbed with V_C compared to V_{CD} in agreement with surface roughness values of valleys and hills of 2 \div 2.2 nm for the rubbing with V_C and 2.5 nm \div 4.8 nm for rubbing with V_{CD} (S_2 and S_3 profiles Fig. 7b). The same behavior was observed for microgrooves profile of **poly (BOCA-pBAPS)** films (sections S_2 and S_3 Fig. 8b). *Conclusion: for the tested films, natural velvet V_C creates deeper and uniform grooves at micro- and nano-level.*

Surface hardness and degree of polymer chains entanglement: decisive influence (through the deformation response which the film exhibit when applying the external mechanical force of friction) restructured surface morphology and thus the orientation of LC deposited on the film surface. The observation is perfectly correlated with morphology results and X-ray diffraction patterns, confirming a lower deformation of the polymer **poly(BOCA-ODA)** - with greater packing - compared to **poly (BOCA-pBAPS)**.

Surface hydrophobicity can be correlated with the restructuring of the film topography during rubbing, because the mechanical rubbing is forcing the polar groups from the film surface to re-orient, leading to changes in local polar moments. How the strength of these dipoles is changed, depends on the structural properties of PI. Polarity changes which have taken place on the surface of the film was evaluated by measuring the water contact angle before and after rubbing with a cloth. Surface roughness and its different chemical characteristics, are the main factors affecting the value of the contact angle. The balance between hydrophobic and hydrophilic PI film surface is measured through the free energy of hydration ΔG_w , parameter calculated using the surface tension of water, γ_{lv} (72.8 mN / m) and contact angle with water on studied samples (Table 3).

By rubbing, surface hydrophobicity increased for all samples, contrary to the literature data. The value of the free energy of hydration - ΔG_w - had the same trend, confirming the relationship of literature $\Delta G_w > -113 \text{ mJ} / \text{m}^2$ characterizing a hydrophobic polymer.

$$\Delta G_w = -\gamma_{lv} \cdot (1 + \cos \theta_{apa})$$

Table 3. Values of contact angle and free energy of hydration

Polymer	Water contact angle (degrees)- θ_{water}	free energy of hydration ($\text{mJ} \cdot \text{m}^{-2}$) - ΔG_w
poly(BOCA-ODA)	90	-73
poly(BOCA-ODA)/V _C	91	-72
poly(BOCA-ODA)/V _{CB}	98	-63
poly(BOCA-pBAPS)	78	-88
poly(BOCA-pBAPS)/V _C	90	-73
poly(BOCA-pBAPS)/V _{CB}	97	-64

Changes in the surfaces wetting features after rubbing may be explained by: * the effect of chains orientation and the rearrangement of polar groups on the film surface during friction; * the chemical structure of the material of the two types of velvet (V_C higher polarity than V_{CD} because of the higher number of hydroxyl groups) responsible for forming hydrogen bonds with the oxygen in the ether, imide and nitrogen atoms; * electrostatic interactions between polar groups of the fabric, and various polar groups on the surface of the film (carbonyl, sulfone, ether); * increasing dispersion character of surfaces due to increased dispersion forces London (generated by fluctuations of electron density in non polar molecules and create instant attraction between dipoles) and Debye (dipole forces between permanent dipoles and induced dipoles). **From the results it can be assumed that predominant electrostatic interactions are those of repulsion that reject the polar groups from the surface.** This hypothesis was verified by EDX analysis for the film surface before and after the rubbing For both samples, the surface topography reorganization after rubbing resulted in: an increase in the C percent (as a possible result of an outward orientation of the polarized double bond C = C from aliphatic cycle of dianhydride) and a downward trend in N and O percents (the possible effect of electrostatic repulsion forces which are pushing functional groups into the polymeric material). Small percentage of sulfur from the film surface **poly (BOCA-pBAPS)** is explained by geometrical constraints of polymer chains, imposed by special configuration of BOCA monomer which generates an increase in free volume, forcing orientation sulfone groups within macromolecular coil.

2.5. Effect of molecular organization induced in polyimide film by LC matrix on the alignment properties. To highlight the effect molecular organization induced by liquid crystalline matrix we studied for comparative purposes the morphology of polyimide precursor / HPC and polyimide / HPC. To achieve mixed alignment layers in this study it was used a PI derived from DOCD and ODA monomers. Figure 13 shows AFM images of these systems in different mixing ratios.

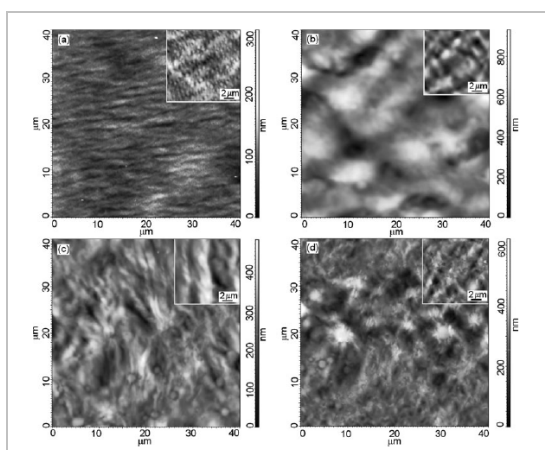


Figure 13. AFM images: (a) 30PAA_{DOCDA-ODA}/70HPC, (b) 70PAA_{DOCDA-ODA}/30HPC, (c) 30PI_{DOCDA-ODA}/70HPC, (d) 70PI_{DOCDA-ODA}/30HPC

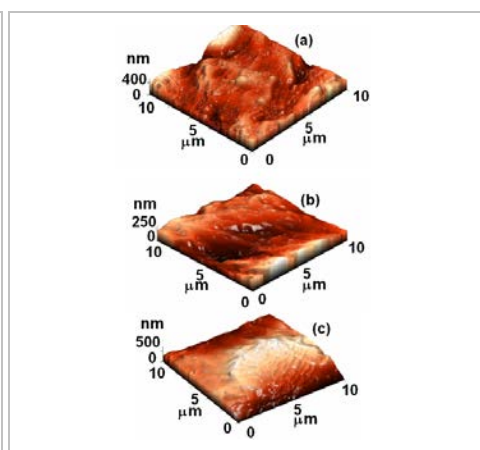
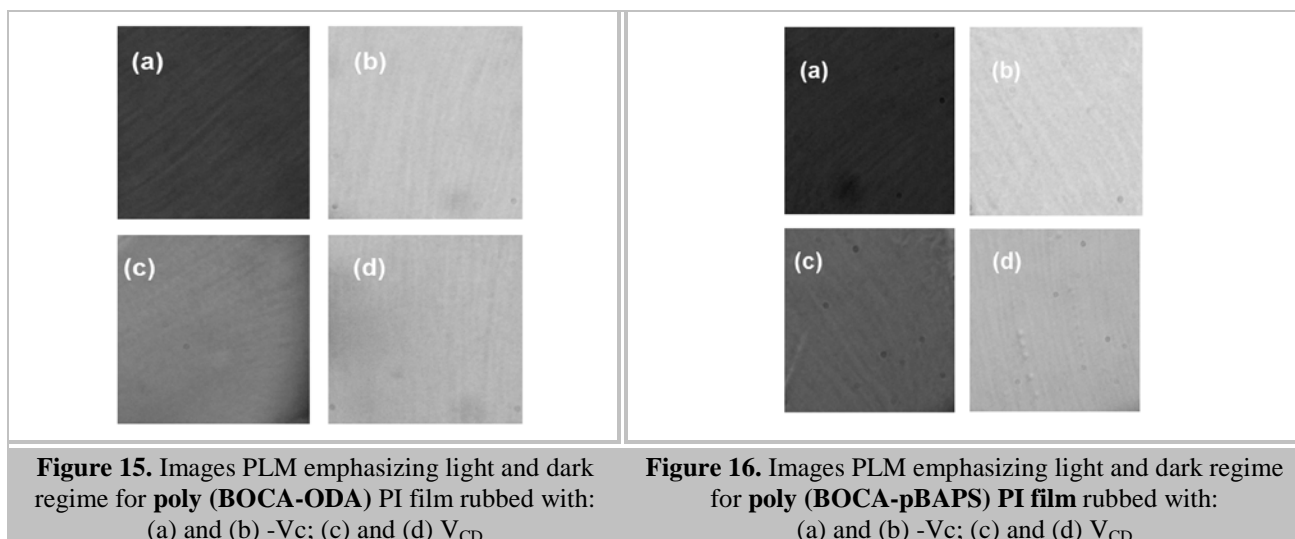


Figure 14. AFM images for PI_{DOCDA-ODA}/HPC films in different mixing reports: (a) 40/60 PI/HPC, (b) 50/50 PI/HPC și (c) 60/40 PI/HPC grav./grav

For PAA_{DOCDA-ODA} / HPC system both sets of bands are obtained at 30/70 mixing ratio (Figure 13), the resulting morphology being stabilized by the formation of hydrogen bonds between the components between them and with the solvent (DMAc). Scanning was performed on a surface area of $10 \mu\text{m}^2$, regardless of the content of HPC, in order to be able to analyze the effect of mixture composition, on the bands structure. Secondary bands are observed only when the percentage of HPC is more than 50 wt%. It should be noted that the uniformity of bands and their size can be adjusted by varying the amorphous component introduced into the system. As the percentage of LC decreases, the surface texture is kept, the size of the bands become higher and the set of secondary texture disappears. For the PI_{DOCDA-ODA} / HPC system, the hydrogen bonds occur mainly between HPC and DMAc, band texture is larger than for PAA_{DOCDA-ODA} / HPC, and increases with reducing the amount of HPC (Figure 14). The morphology of the film is influenced by the composition of the mixture, PAA or PI, the rate of evaporation of the solvent, the film thickness and the duration of shearing.

The results show that both the PAA and the PI-based on DOCDA dianhydride may be used as alignment layers because their more flexible structure in relation to the liquid crystalline component, allows stabilization optical states and a good control on the morphology, the topographic features being essential in obtaining alignment layers for LCs.

2.6. Testing of liquid crystal films deposited on hPI for applications as alignment layers. The mechanism of orientation of LC molecules at the surface of the PI film morphologically reorganized by friction, is highly dependent on complex interactions polymer-LC, which include van der Waals interactions, dipole interactions, steric factors, hydrogen bonds to the surface of the film, the chemical composition of the two components and surface topography. Literature studies propose two alignment mechanisms that explain anchoring of LC molecules: *anisotropic LC orientational elasticity in connection with an induced surface pattern; *short-range interactions on the molecular scale. For PI films under study, the induced alignment mechanism can be placed in the first category, without neglecting the interactions that occur at the interface between the imide ring and LC molecules [N-(4-methoxybenzylidene)-4-butylaniline] - MBBA]. Carbonyl groups, more polar than CN imide linkages, along with ether bridges (from diamine) with partially polar character can interact with LC, having a positive contribution to alignment. MBBA molecules are therefore oriented at the PI film surface due to a cumulative effect of dipole-dipole interactions and hydrogen bonds. Testing of LC alignment was performed in polarized light having two crossed polarizing filters, between which the sample is rotated 360° to observe the changes light intensity. We obtained for both PI films dark regions for a rotation of the plane of incident polarized light at 0° and 90° (indicating an alignment parallel to the transmission direction of the polarizer) and a maximum illumination of the visual field of microscope at an angle of 45° and 135° , respectively (Figures 15, 16).



The strong contrast between light and dark images reveals uniform alignment of LC. Rubbed PI films with artificial velvet, V_{CD}, shows a lower contrast compared with those rubbed with natural velvet, in agreement with the AFM images obtained for both samples. There is a slight unevenness of the surface rubbed with V_{CD} films. The degree of alignment, estimated by comparing the contrast, was higher for poly(BOCA-pBAPS) rubbed with V_c. *Considering that the films analyzed are practically colorless, with excellent transparency in visible domain, it can be concluded that the polyimide poly(BOCA-pBAPS) is a very good polymer that can be used as a substrate for LC alignment.*

All objectives were fully realized in this stage.

A part of this results were included into some scientific papers submitted to publication and a PhD thesis.

Results dissemination

- 3 papers published in journal indexed by web of knowledge
- 1 paper published in volume of international conferences
- a book chapter
- a PhD thesis
- The team members participated at 6 scientific events with 2 oral presentations and 9 posters

Published / accepted papers in journals with impact factor

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* , [DOI 10.1002/pen.23260](https://doi.org/10.1002/pen.23260)

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