

Spectral Study of Oriented Nanostructured Surfaces of Some Polymers Functionalized with Monochlorotriazinyl- β -cyclodextrin

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This paper presents the practical strategies of obtaining the oriented nanostructured surfaces of some polymers functionalized with monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) by uniaxial rubbing. We have chosen for the present study three polymers (copoly(styrene-allyl alcohol), poly-4-vinylphenol, polyvinyl alcohol) with hydroxyl groups allowing the grafting of the reactive product monochlorotriazinyl- β -cyclodextrin. The obtained oriented nanostructures align colourless nematic liquid crystals (NLC) or NLC coloured with a dichroic dye. The orientation of NLC has been studied by means of polarized light FT-IR spectroscopy (IR dichroism) and polarized light UV-Vis spectroscopy (Vis dichroism). For poly-4-vinylphenol, both the initial polymer and the chemically modified product have an exotic behaviour with regard to the ability of orientating the NLC, namely perpendicularly to the rubbing direction.

Keywords: monochlorotriazinyl- β -cyclodextrin, copoly(styrene-allyl alcohol), poly-4-vinylphenol, polyvinyl alcohol, oriented nanostructured surface, nematic liquid crystal

New materials for applications in biology, biochemistry, medicine, physics, opto-electronics etc. can be obtained modifying the surfaces by techniques allowing the control at molecular level of the substrate properties.

The oriented nanostructured surfaces can be studied with nematic liquid crystals (NLC) that are aligned by the superfine details. The most known methods of obtaining the nanostructures are:

- uniaxial rubbing of the polymer surfaces [1]. After rubbing, most of the polymers, so-called common, form oriented nanostructures whose details, parallel to the rubbing direction, align in the same manner NLC. But there are several polymers, so-called special polymers or polymers with exotic behaviour (with side chains containing nonsaturated nuclei - polystyrene, poly-4-vinylpyridine, poly-4-vinylphenol, poly-N-vinylimidazole etc.) which, after rubbing, orient NLC perpendicularly to the rubbing direction [2-4]. The finest oriented nanostructured traces of these polymers are perpendicular to the rubbing direction;

- rubbing a polymer cylinder against a surface heated at the polymer softening temperature [5-8]. The polymeric material passes from the cylinder to the solid support (e.g. glass), leading to a oriented nanostructured surface with traces parallel to the rubbing direction and NLC orient inside these traces also parallel to the rubbing direction;

- oblique vacuum evaporation of dielectric materials (e.g. silicium dioxide - SiO₂) at angles varying from 45 to 80 degrees on solid supports (glass, quartz, metals) [9-11]. Parallel rows of columns, perpendicular to the plane of incidence of the vapour, are formed. These deposits as such, or covered with polymer nanofilms, orient NLC parallel to the rows of columns;

- linearly polarized UV light irradiation of photosensitive polymers [1, 11-17]. NLC orient perpendicularly to the light polarization plane, the oriented nanostructured details, that appear after irradiation, being perpendicular to the light polarization plane, too;

- nano-rubbing of a polymer film surface with an AFM cantilever tip [18]. NLC orient parallel to the tip advance direction in the resulting nano-ripples;

- repeated scanning of an exotic polymer film with an AFM cantilever tip, using the non-contact method [19, 20], leading to nanostructures perpendicular to the scanning direction. These nanostructures can orient NLC perpendicularly to the scanning direction.

The present paper has studied method of obtaining oriented nanostructured surfaces.

Such nanopatternings are promising systems for potential medical application, namely for the detection and the identification of pathogenic agents (e.g., viral antigens), based on the inclusion compounds of cyclodextrins with bioactive substances. The avidin-biotin system, used as a model for the study of the antigen-antibody interactions, is a good example [21-24].

Experimental part

Materials and methods

The following compounds have been used as starting materials:

- reactive host compound: monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) from Germany;

- polymers: copoly (styrene-allyl alcohol) (Aldrich), poly-4-vinylphenol (Aldrich), polyvinyl alcohol;

- solvents (spectroscopic grade): chloroform (Merck), dimethyl sulfoxide (DMSO) (Fluka), acetone (Merck);

- nematic liquid crystals (NLC): ZLI 1132 (Merck; mixture of NLC with cyano-phenyl-cyclohexane-alkyl and cyano-biphenyl-cyclohexane-alkyl structures) and red coloured ZLI 1842 (Merck; mixture of NLC with red dichroic dye);

- supports for the polymer films: glass sheets, quartz and KRS5 windows (TII, TIBr);

- UV-Vis polarizer film (800 - 280nm);

- IR polarizer with wire gold grid (5000-300 cm⁻¹) (USA).

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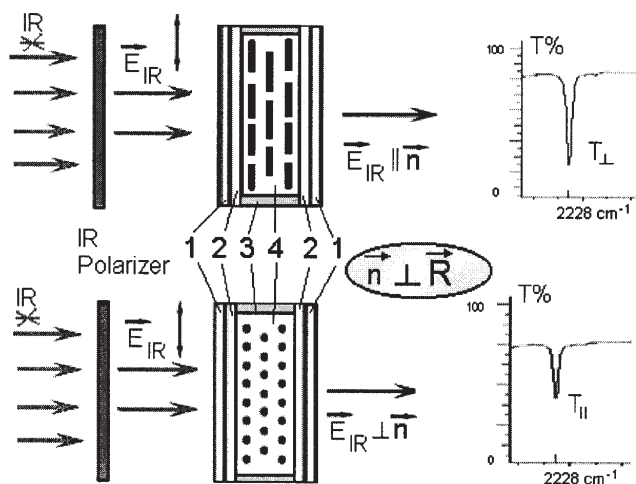


Fig. 1. FT-IR study (with LPIRL – IR dichroism) of the NLC alignment by the special polymer films stressed by uniaxial rubbing (R): 1 – KRS5 window; 2 – polymer film (0.3- 0.5 μm); 3 – spacer (25 μm); 4 – NLC layer (ZLI 1132); n – NLC director vector; E_{IR} – IR polarization direction (the electric vector of LPIRL)

Sample preparation

Polymer functionalization with MCT- β -CD

100 mg of each polymer and 50 mg of MCT- β -CD have been dissolved in 10 mL of DMSO; the resulting solution is kept under vigorous stirring (magnetic stirrer; 1000 RPM) for 10 h at 90°C. After this treatment, the -OH groups of the monomer units react with the reactive chlorine of MCT- β -CD. For the reaction massic ratio polymer: MCT- β -CD = 2:1, the final product contains 3-5 monomer units grafted with triazinyl- β -CD.

The obtaining of the polymer films and the oriented nanostructured surfaces

The solutions of the initial polymers and the ones of the functionalized polymers in adequate solvents (DMSO, chloroform, water, acetone) have been deposited on solid supports (glass sheets and quartz windows for UV-Vis studies; KRS5 windows for FT-IR studies), centrifugally homogenized using the spin-coating method (1500 RPM) and then dried with a warm air jet at 75°C, for 15 min. In order to remove the solvent traces from films, the samples have been placed inside a vacuum drying closet at 110°C, for 4 h. The solid films of 5-10 μm (with several non-uniformities in thickness) obtained on supports have been used to confirm the grafting reaction (by FT-IR spectroscopy).

Ultrafine films of 0.3-0.5 μm can be obtained by diluting the previous solutions (increasing the solvent share seven times). These films have been used to confirm the grafting reaction (by UV-Vis spectroscopy) and, after their nanostructuring, for the study of the interaction with NLC (by Vis and FT-IR dichroism). The film thickness was determined spectrally or gravimetrically.

The oriented nanostructuring of the functionalized polymer surfaces (that induces the NLC alignment) was realized by uniaxial rubbing (mechanical stress) with a home-made machine.

Materials characterization

FT-IR spectroscopy. The FT-IR analysis was performed with a JASCO 6001 FT-IR (Japan) and an IR Affinity SHIMADZU (Japan) spectrophotometer (in the range 4000-600 cm^{-1}). FT-IR spectra registered with linearly polarized IR light (LPIRL) have been obtained with an IR polarizer (a wire gold grid on a window of KRS5).

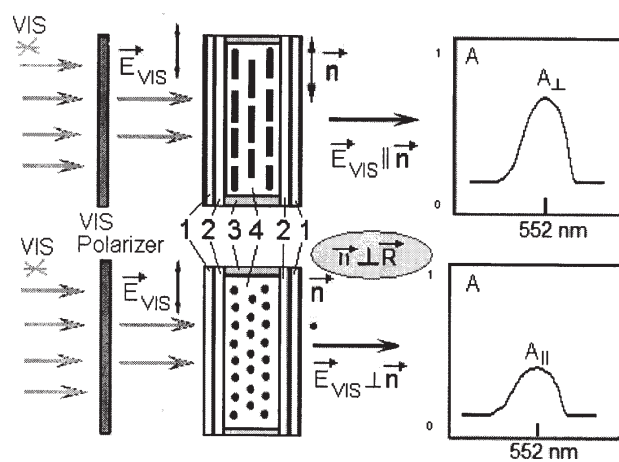


Fig. 2. Vis spectroscopy study (with linearly polarized light – Vis dichroism) of the NLC alignment by the polymer special films stressed by uniaxial rubbing (R): 1 – quartz (or glass) window; 2 – polymer film (0.3-0.5 μm); 3 – spacer (25 μm); 4 – NLC (ZLI 1842) layer with a red dichroic dye; n – NLC director vector; E_{VIS} – Vis polarization direction (the electric vector of LPVISL)

The principle of the IR dichroism investigation of the NLC orientation by the oriented nanostructured surfaces of the polymers mechanically stressed is presented in figure 1. The different values of transmittance (for the IR absorption band at 2228 cm^{-1} , assigned to the -CN group) indicate the orientation of the NLC induced by the special polymer films. The orientation of a NLC molecule (and, respectively, the one of the layer it belongs to) is the same with the one of the transition moment of the -CN group from NLC. The axis of the molecule is parallel to n – NLC director vector of the oriented layer.

UV-VIS spectroscopy

The UV-Vis analysis has been realized with an UV-Vis Specord 250PC spectrophotometer (Germany) in the range 190-1100 nm. The Vis spectra registered with linearly polarized Vis light (LPVISL) have been obtained with a polarizer film - Polaroid HNP'B.

The investigation scheme of using the Vis dichroism of the NLC orientation by the oriented nanostructured surfaces of the polymers after uniaxial rubbing is presented in figure 2. The absorbance different values (for the Vis absorption band at 552 nm, assigned to the chromophore of the dichroic dye from the red coloured NLC) indicate the orientation of the NLC induced by the special polymer films (mechanically stressed). The orientation of a NLC molecule (and, respectively, the one of the layer it belongs to) is the same with the one of the dichroic dye molecule. The axis of the molecule is parallel to n – NLC director vector of the oriented layer.

Results and discussions

Polymer functionalization with MCT- β -CD

FT-IR analysis

The IR absorption bands characteristic for MCT- β -CD [25, 26] are also present in the FT-IR spectra of the grafted products polymer-MCT- β -CD (table 1).

- Copoly(styrene-allyl alcohol)-grafted with MCT- β -CD

The IR absorption bands characteristic to MCT- β -CD (fig. 3, spectrum C; 1408, 1317, 1153, 1025, 946, 810 cm^{-1}) are present in the spectrum B of the grafted copolymer (fig. 3; 1412, 1301, 1142, 1030, 946, 806 cm^{-1}), showing that the reaction has taken place.

Position cm^{-1}	Symbol	Assigning	Observations
• 1610	$\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{N})$	In- plane stretching (valency) vibrations of the $\text{C}=\text{N}$ and $\text{C}-\text{N}$ groups	▪ = specific to the cycle of β -CD from MCT- β -CD [$\nu(\text{C}-\text{O}-\text{C})$, $\delta(\text{OH})$, $\nu(\text{C}-\text{OH})$] • = specific to the triazinic ring
• 1537			
• 1489			
• 1408			
1317			
▪ 1153	$\nu(\text{C}-\text{O})$	Stretching (valency) vibrations of the $\text{C}-\text{O}$ group	
▪ 1080	$\nu(\text{C}-\text{O})$ $\delta(\text{OH})$ $\nu(\text{C}-\text{Cl})$	Stretching (valency) vibrations of the $\text{C}-\text{O}$ group Deformation vibrations of the $-\text{OH}$ group Stretching (valency) vibrations of the $\text{C}-\text{Cl}$ group	
▪ 1025	$\delta(\text{OH})$	Deformation vibrations of the $-\text{OH}$ group	
▪ 946			
• 810	$\delta(\text{triazinyl})$	Deformation of the triazinic ring	
788			
▪ 768			
▪ 709			

Table 1
THE ASSIGNING OF THE FT-IR
ABSORPTION BANDS CHARACTERISTIC
FOR MCT- β -CD

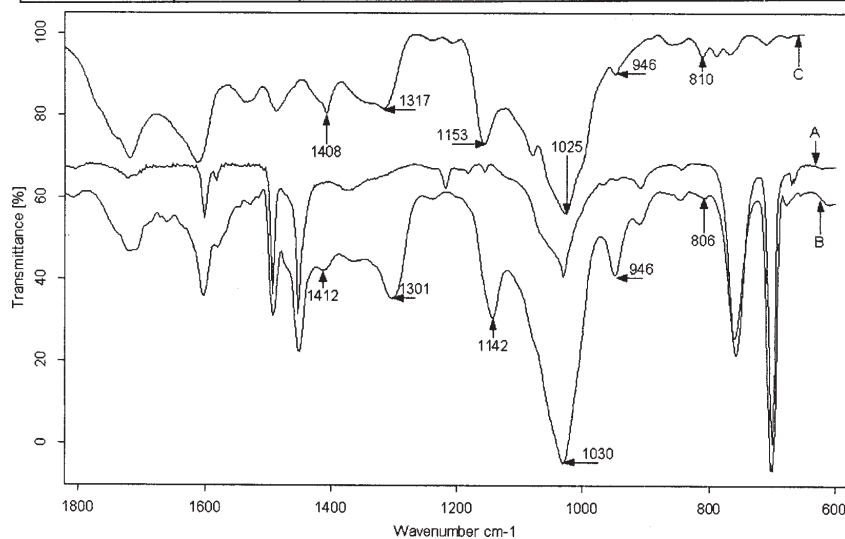


Fig. 3. FT-IR spectra ($1800-600 \text{ cm}^{-1}$):
A=copoly(styrene-allyl alcohol) (film from chloroform); B=copoly (styrene-allyl alcohol) - MCT- β -CD (film from DMSO); C= MCT- β -CD (in KBr)

- Poly-4-vinylphenol-grafted with MCT

The IR absorption bands characteristic to MCT- β -CD (fig. 4, spectrum C; $1153, 1080, 946, 788, 768 \text{ cm}^{-1}$) are present in the spectrum B of the grafted polymer (fig. 4; $1144, 1080, 948, 787, 760 \text{ cm}^{-1}$), being a proof of the reaction.

- Polyvinyl alcohol – grafted with MCT- β -CD

The IR absorption bands characteristic to MCT- β -CD (fig. 5, spectrum C; $1610, 1153, 1025, 810, 788, 768, 709 \text{ cm}^{-1}$) are present in the spectrum B of the grafted

copolymer (fig. 5; $1610, 1152, 1030, 810, 789, 758, 705 \text{ cm}^{-1}$), showing that the reaction has taken place.

UV analysis of film on quartz window

- Copoly(styrene-allyl alcohol) – grafted with MCT- β -CD

The absorption band of the triazinic nucleus in MCT- β -CD at 221 nm (fig 6, spectrum D) is also present in the subtraction spectrum C of the grafted polymer (fig. 6), demonstrating the presence of MCT- β -CD in the reaction product.

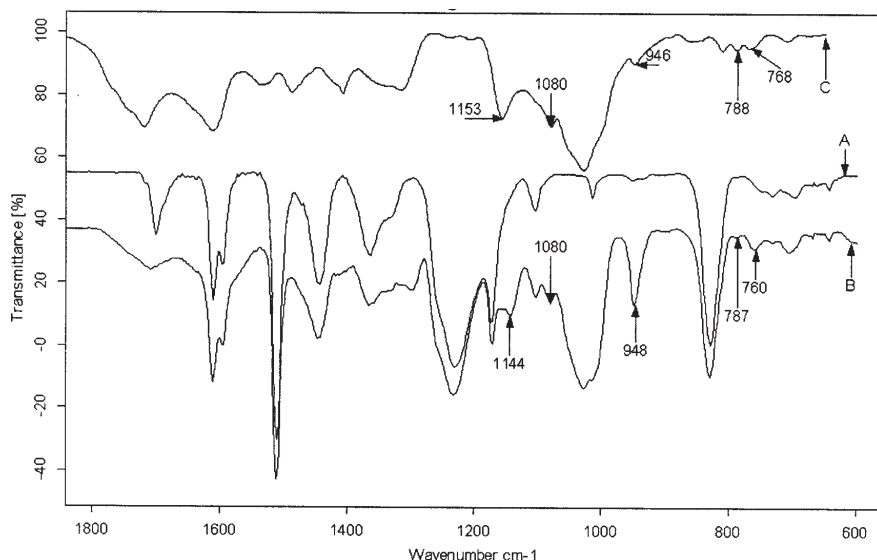


Fig. 4. FT-IR spectra ($1800-600 \text{ cm}^{-1}$):
A= poly-4-vinylphenol (film from acetone); B= poly-4-vinylphenol - MCT- β -CD (film from DMSO); C= MCT- β -CD (in KBr)

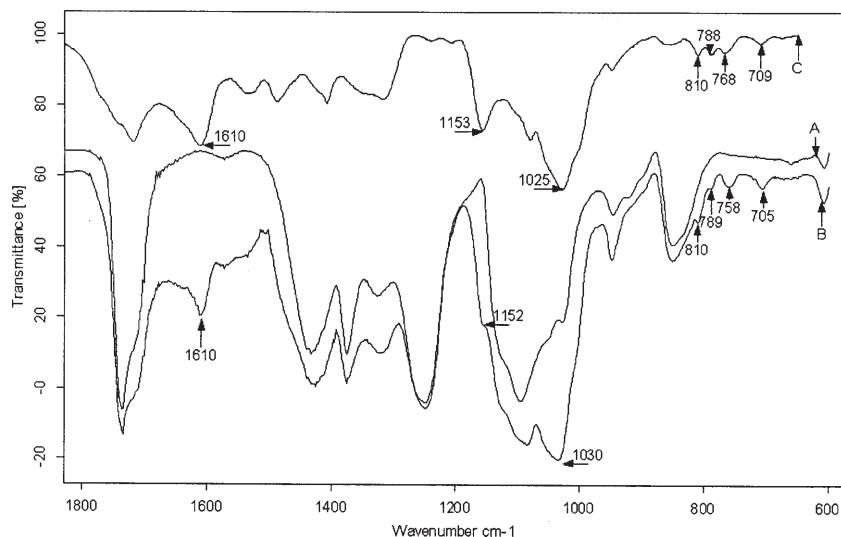


Fig. 5. FT-IR spectra (1800-600 cm^{-1}): A=polyvinyl alcohol (film from water); B = polyvinyl alcohol - MCT- β -CD (film from water); C = MCT- β -CD (in KBr)

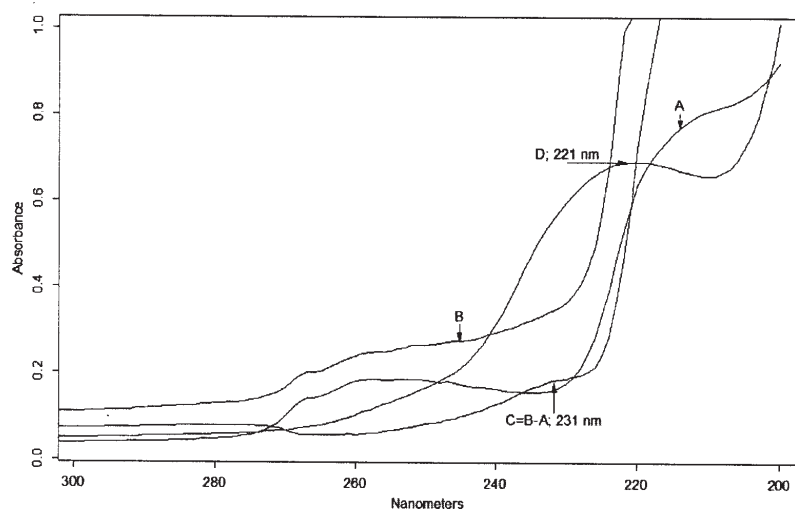


Fig. 6. UV spectra (300-200 nm): A= copoly(styrene-allyl alcohol) (film from chloroform); B=copoly(styrene-allyl alcohol)-MCT- β -CD (film from DMSO); C = B-A = (copoly(styrene-allyl alcohol)-MCT- β -CD) - copoly(styrene-allyl alcohol); D=MCT- β -CD (solution in water)

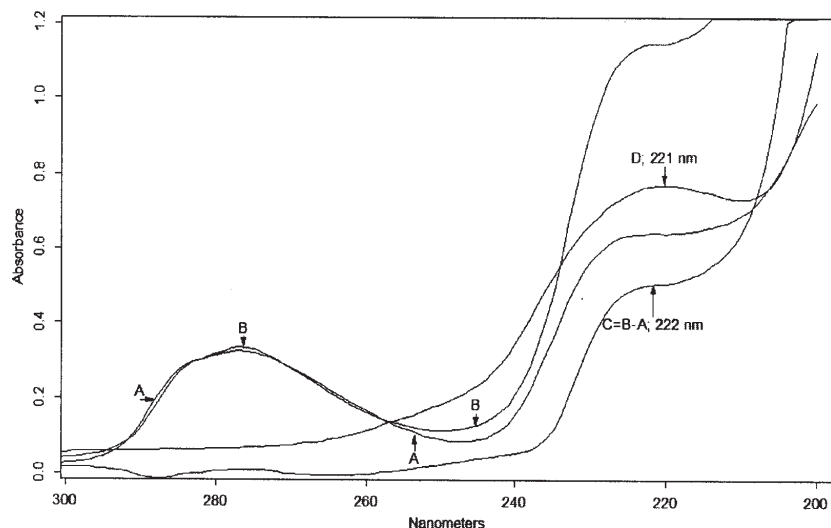


Fig. 7. UV spectra (300-200 nm): A= poly-4-vinylphenol (film from acetone); B= poly-4-vinylphenol -MCT- β -CD (film from DMSO); C=B-A= (poly-4-vinylphenol -MCT- β -CD) - poly-4-vinylphenol; D=MCT- β -CD (solution in water)

- Poly-4-vinylphenol – grafted with MCT- β -CD.

The absorption band of the triazinic nucleus in MCT- β -CD at 221 nm (fig 7, spectrum D) can also be found in the subtraction spectrum C of the grafted polymer (fig. 7).

-Polyvinyl alcohol – grafted with MCT- β -CD

The absorption band of the triazinic nucleus in MCT- β -CD at 221 nm (fig. 8, spectrum D) can also be found in the subtraction spectrum C of the grafted polymer (fig. 8).

Study of nanostructured polymer surfaces by uniaxial rubbing.

A possible scheme of the oriented nanostructures formation by uniaxial rubbing for the polymers with special

behaviour (copoly(vinylcinnamate-vinylalcohol)- MCT- β -CD) and its confirmation by AFM technique are presented in figure 9 [27].

Subsequent to the mechanical stress by uniaxial rubbing, the films of the polymers copoly(styrene-allyl alcohol), poly-4-vinylphenol, polyvinyl alcohol grafted with MCT- β -CD, have oriented nanostructures that align colourless NLC, alignment studied and evidenced by polarized light FT-IR spectroscopy (FT-IR dichroism, fig. 10 a, b, c). The registration of the FT-IR absorption values in absorbance (fig. 10 d, e, f) has been made in the domain 0-360°, rotating the IR polarizer (respectively, E_{IR} – IR polarization direction (the electric vector of LPIRL)) as against the rubbing direction R (respectively, n – NLC director vector) with a 5° step.

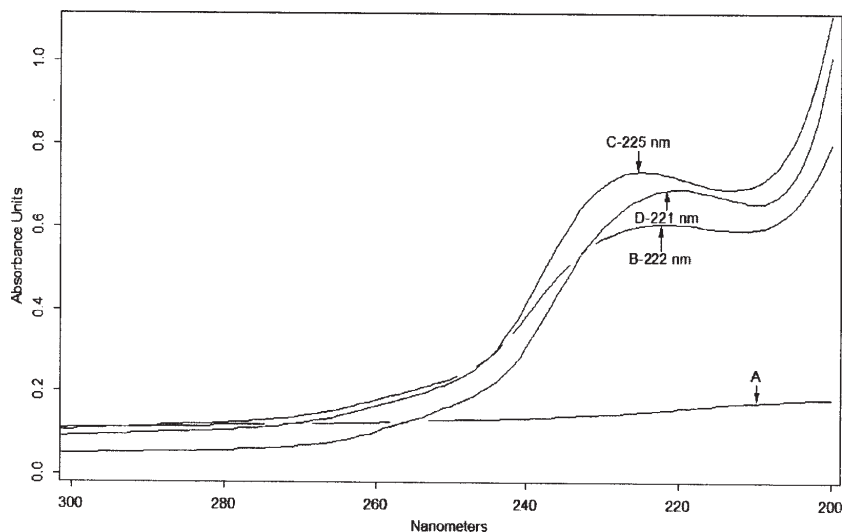


Fig. 8. UV spectra (300-200 nm): A= polyvinyl alcohol (film from water); B= polyvinyl alcohol - MCT- β -CD (film from water); C=B-A= (polyvinyl alcohol -MCT- β -CD) - polyvinyl alcohol; D=MCT- β -CD (solution in water)

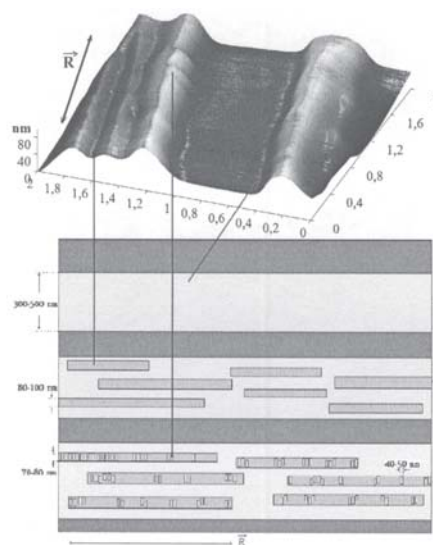


Fig. 9. The formation of the nanostructures oriented of a parallel manner (fine tracks 2 and 3), respectively perpendicular (superfine tracks 4) on the uniaxial rubbing direction (R) of the special polymer film (1) (covering the glass sheet or the KRS5 window), after mechanical stress. For common polymers there are only fine tracks 2 and 3

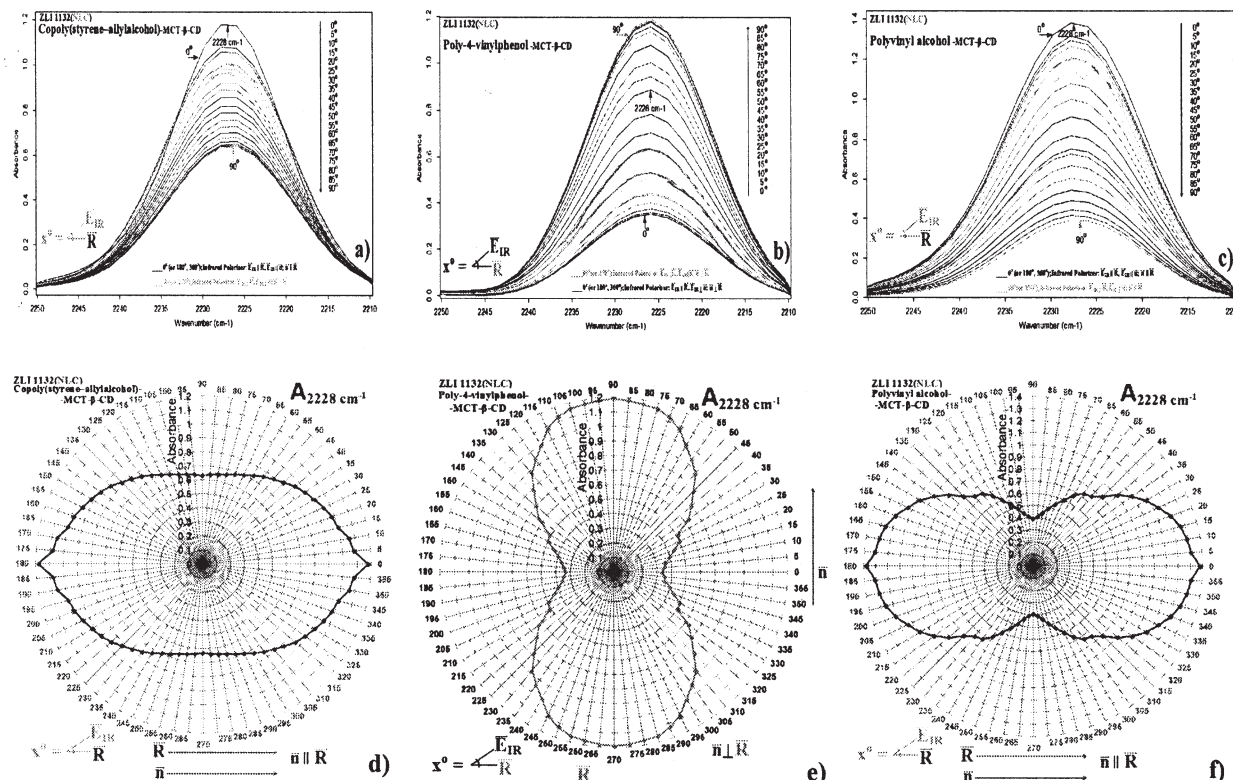


Fig.10. The alignment of colourless NLC (ZLI 1132) (evidenced by the vibration of the cyan -Ca \equiv N group) induced by the surface of the mechanically stressed polymers grafted with MCT- β -CD (copoly(styrene-allyl alcohol) - a, d; - poly-4-vinylphenol- b, e; polyvinyl alcohol - c, f); a, b, c - FT-IR spectra of the NLC oriented by polymers; d, e, f- polar diagrams

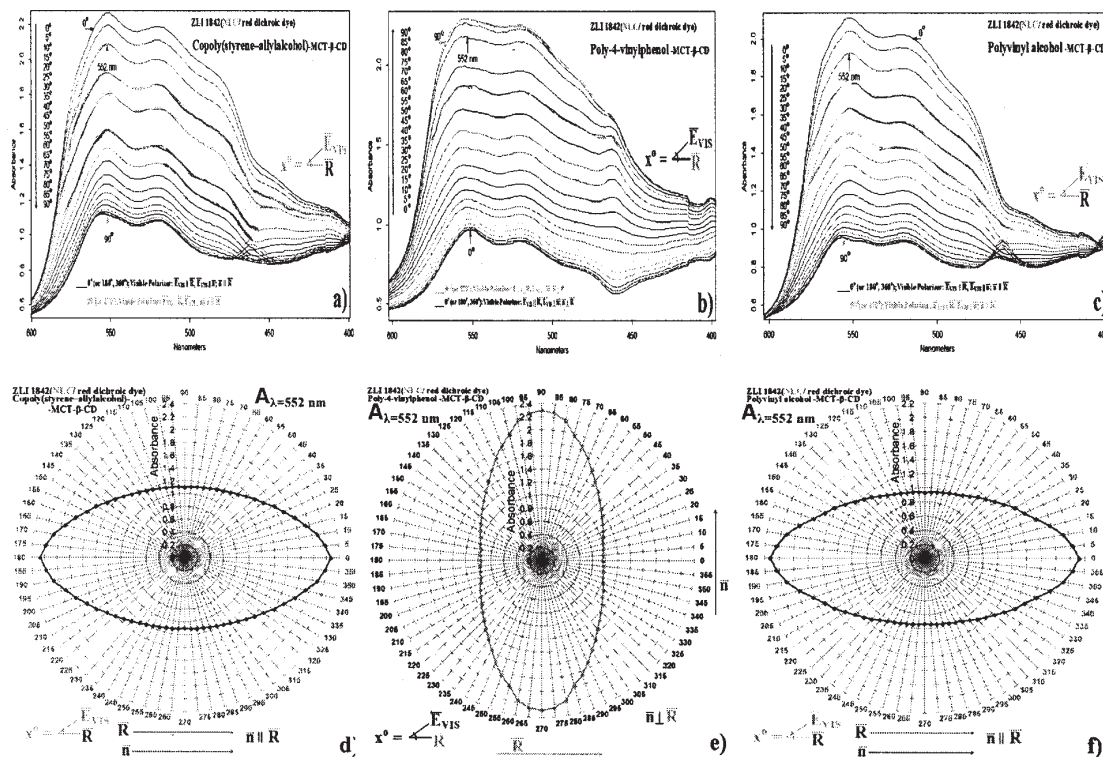


Fig.11. The alignment of NLC (ZLI 1842 - NLC with red dichroic dye), (evidenced by the orientation of dichroic dye molecules) induced by the surface of the mechanically stressed polymer grafted with MCT- β -CD (copoly(styrene-allyl alcohol) - a, d; - poly-4-vinylphenol- b, e; polyvinyl alcohol - c, f): a, b, c - Vis spectra of the NLC oriented by polymers; d, e, f- polar diagrams

The polymer poly-4-vinylphenol - MCT- β -CD presents a special behaviour, orienting the NLC molecules (n - NLC director vector) perpendicularly to the uniaxial rubbing direction [2-4]. For the other 2 polymers the effect is reverse (polymers with common behaviour).

Similarly to the polarized light FT-IR study, polarized light Vis spectroscopy (Vis dichroism, fig. 11 a, b, c) was used to evidence the alignment of coloured NLC by the oriented nanostructures (formed subsequent to the mechanical stress) of the 3 polymer films grafted with MCT- β -CD. The registration of the Vis absorption values in absorbance (fig. 11 d, e, f) has been made in the domain 0-360°, rotating the Vis polarizer (respectively, E_{vis} - Vis polarization direction (the electric vector of LPVISL)) as against the rubbing direction R (respectively, n - NLC director vector) with a 5° step.

The VIS study also confirms the fact that poly-4-vinylphenol grafted with MCT- β -CD presents a special behavior, orienting the NLC molecules (n - NLC director vector) perpendicularly to the uniaxial rubbing direction R. For the other 2 polymers the effect is reverse (polymers with common behavior).

The modified shape of the polar diagrams corresponding to the FT-IR and Vis studies is due to the differences in method, investigation apparatus, types of polarizers and NLC that have been used.

Conclusions

The functionalization of the studied polymers was realized by the condensation reaction of the hydroxyl groups from the initial polymers with the chlorotriazinyl group of MCT- β -CD. The polymer modification was evidenced by FT-IR and UV-Vis spectroscopy.

Only the aromatic ring containing polymer (*poly-4-vinylphenol*) functionalized with MCT- β -CD presents a special behaviour (NLC orientation perpendicular to the rubbing direction), generating (by *uniaxial rubbing*) oriented

nanostructured surfaces with superfine tracks perpendicular to the uniaxial rubbing direction.

The other 2 polymers (*copoly(styrene-allyl alcohol)* and *polyvinyl alcohol*) functionalized with MCT- β -CD present a common behaviour (NLC orientation parallel to the rubbing direction), generating oriented nanostructured surfaces with fine tracks parallel to the uniaxial rubbing direction.

Oriented nanostructured surfaces align the NLC, phenomenon studied by polarized light FT-IR spectroscopy (IR dichroism) and polarized light Vis spectroscopy (Vis dichroism).

As potential applications, the obtained oriented nanostructures aligning NLC can be used in producing micro- and nanosensors for medical diagnosis. By their specific reaction to macromolecules - e.g. antibodies -, small molecule compounds - e.g. antigens- (included in the nanocavities of MCT- β -CD that functionalize the polymer) modify the initial nanostructuration and, respectively, the NLC alignment.

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