

Dedicated to Acad. Prof. Dr. Margareta Giurgea with the occasion of her 90-th anniversary

PECULIAR ORIENTATION OF NEMATIC LIQUID CRYSTALS ON RUBBED POLYVINYLIMIDAZOLE

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Alignment properties of rubbed films of polyvinyl imidazole were studied by observing with the polarizing microscope the features of the nematic liquid crystal (LC) droplets onto these layers. It was found that the observing of the droplets can reveal the direction of easy axis on the alignment substrate not only in the case of LC having the director normal to the LC/air interface but also in the case of the director tangent to this interface, when no disclination line could be seen. We observed that some of the LCs are oriented parallel to the rubbing direction, but the other LCs are perpendicularly oriented. This peculiar behavior is at variance to that found on rubbed layers of polyvinyl alcohol. The role of the end-groups in the structure of the LCs on the alignment properties is discussed.

(Received July 4, 2005; accepted July 21, 2005)

Keywords: Nematic liquid crystals, Alignment layers, Rubbed polyvinyl imidazole, Cyan end-group, Methoxy end-group

1. Introduction

Rubbing of the polymer films was imposed as the most widely technique to align liquid crystals in the display devices. However, the detailed mechanism was not yet fully understood. Two models have been proposed to explain the effects of rubbing on the polymer surface and hence on the alignment. On one hand, Berreman [1,2] suggested that the alignment be caused by microgrooves, which were produced by rubbing, evidence for these microgrooves being provided later by electron microscopy. On the other hand, Castellano [3] proposed that the rubbing process caused the partial melting of the top few molecular layers of the polymer which then became oriented parallel with the applied shear field. Orientation of the liquid crystal occurs through molecular level interactions between the oriented polymer and the liquid crystal. Kikuki et al. [4] proved by buffing polymer films at very slow velocity, which cannot cause any significant frictional heating that the polymer surface could be mechanically deformed without softening or melting. Besides, it was also found that the LC is aligned perpendicularly to the rubbing direction (polystyrene derivative films) [5-7].

Several polymers with vinyl backbone and different side groups were thus used for the liquid crystal orientation (e.g. [8,9]). Moreover, Yamaguchi et al. [9] supposed that the alignment direction of the nematic LCs depends on the core structure: the interactions of their core with the substrate prevail on the interactions of their end-groups (like alkyl, alkenyl, cyan or fluorine substituted groups) with the substrate.

In this work we report on the peculiarities of the alignment of some nematic LCs on polyvinyl imidazole (PVI), a sided polyvinyl polymer. We found an example of a couple of LCs, which are aligned differently (one is parallel and the other, perpendicular to the rubbing direction) on rubbed polyvinyl imidazole but similarly (both are parallel to the rubbing direction) on rubbed polyvinyl alcohol. The intriguing aspect of these observations comes from the related structure of

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these LCs differing only by one of their terminal groups. This example is discussed in connection with the complex problem of the interaction of liquid crystals with the polymer substrates.

2. Experimental

2.1 Materials

LCs and the substrates were chosen to allow observing different alignments. Two polymers with the vinyl backbone were used for alignment substrate: polyvinyl alcohol (PVA) and polyvinyl imidazole. The former has well-known orientational properties [5] while the other has a less studied behavior [8]. PVI was prepared in laboratory by radical polymerization of vinyl monomer (Aldrich) [8] whereas PVA was obtained from Aldrich. Commercially available nematic liquid crystals with cyan, methoxy or alkyl end-groups were used: Their characteristics are presented in Table 1.

2.2 Alignment layers

These were obtained by spinning the polymer solution (1.5 w% in water) on float soda lime glass plates cleaned previously. After deposition, the layers were thermally treated at 120 °C for a couple of hours. Polymeric layers were then unidirectionally rubbed with a home made machine.

The glass plates were used as such or assembled in cells so that the rubbing directions of the two plates are antiparallel. One of these plates was deposited with a layer of PVA as reference alignment. Mylar spacers of 15 μm ensured the control of the cell thickness.

2.3 Investigation methods

To detect the direction of the easy axis imposed by the alignment layer, the optical transmission images of a nematic LC droplet onto the layer were observed with the optical microscope, under parallel polarizers.

Additionally, the orientational properties of the alignment layers were studied by looking for the features of the LC cells under microscope. The scheme of the observation experimental set-up is given in Fig. 1.

Table 1. Nematic liquid crystals and their main characteristics.

LC label	Composition	Acronym	Temperatures of phase transitions* /°C	Dielectric anisotropy	Purchased from
LC1	methoxybenzilidenebutylaniline	MBBA	C 22 N 42 I	$\Delta\epsilon < 0$	Aldrich
LC2	p-[N-(p-methoxybenzilidene)-amino]phenyl acetate		C 79 N 102 I	$\Delta\epsilon < 0$	Eastman Kodak
LC3	p-[N-(p-methoxybenzilidene)-amino] phenylbenzoate		C 120 N 164 I	$\Delta\epsilon < 0$	Eastman Kodak
LC4	methoxyphenyl pentylcyclohexyl carboxylate	CM-1951	C 41.5 N 72.7 I	$\Delta\epsilon < 0$	La Roche
LC5	4n-pentyl-4'-cyanobiphenyl	5CB	C 24 N 35.5 I	$\Delta\epsilon > 0$	Aldrich
LC6	cyanophenyl pentylcyclohexyl carboxylate	CM-1850	C 47.5 N 80.5 I	$\Delta\epsilon > 0$	La Roche
LC7	cyanophenyl pentylbenzoate	PE	C 64 (N 55.4) I	$\Delta\epsilon > 0$	La Roche
LC8	pentylphenyl pentylbenzoate		C 33.1 (N 25.4) I	$\Delta\epsilon > 0$	La Roche

*C- crystalline; N- nematic; I- Isotropic.

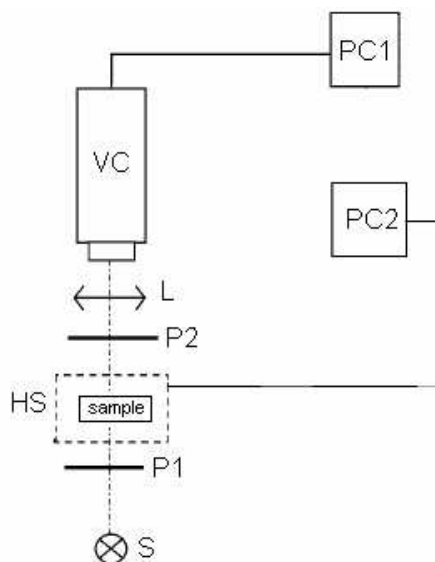


Fig. 1. Scheme of observation set-up: S- light source, P1 – polarizer, P2 - analyzer, HS – hot stage (Instec, Inc), L – microscope optical system, VC – video camera (Commax CRC 41CP), PC1 – PC for image acquisition, PC2 – PC for stage control.

3. Results and discussion

Relevant micrographs of the droplets of the studied nematic LCs onto the plates covered with alignment layers are shown in Fig. 2. Disclination lines can be observed in all these micrographs, either parallel or perpendicular to the rubbing direction (shown by an arrow in this figure). The alignment obtained is rather stable in time (at least for several months) and also by increasing the temperature (to tens of degrees).

It is known [10] that for a nematic LC having the director perpendicular to the LC/air interface, a disclination line is generated inside the droplet (observed between polarizers), which gives information about the direction of easy axis, about the existence of a pretilt angle and about the azimuthal anchoring strength. When the pretilt angle is close to zero, this disclination line appears across the center of the LC droplet; it is perpendicular to the easy axis [10]. This is the case of many investigated systems.

According to these findings, LC5 (5CB) and LC1 (MBBA) on PVA substrate are oriented along the rubbing direction, as expected [5], while on PVI 5CB is oriented perpendicular to the rubbing direction on PVI and MBBA is also oriented along the rubbing direction. One can see in Fig. 2 that other nematic LCs, having either cyan (CN) end-group or methoxy end-group behave similarly to these onto the two alignment substrates.

We extended this method to identify the easy axis (the direction imposed by the alignment surface) for the nematic LC having the director tangent to the LC/air interface. In such a case, a disclination line cannot be seen when the droplet is observed between parallel polarizers. The droplet behaves as a lens with the focus length depending on the orientation of the easy axis imposed by the substrate against the polarizer orientation. When the polarizer direction coincides with the molecular alignment the droplet refractive index coincides with the LC extraordinary index, while the droplet refractive index has the value of the LC ordinary refractive index for orientation of polarizing direction normal to the LC alignment direction. Arguments from geometrical optics indicate that in the former case the central bright region of the droplet image is much more restricted than in the latter case (Fig. 3). More details on the extension of the Yamaguchi and Sato's method are given elsewhere [11].

Table 2 summarizes the observed alignment properties of studied substrates. It is noteworthy that on PVI substrate, the LC having molecules ending with cyan group is oriented normally to the

rubbing direction. At the same time, the more polar and flexible groups like methoxy groups seem to determine a parallel alignment. In the case of alkyl tails, one observes a perpendicular alignment.

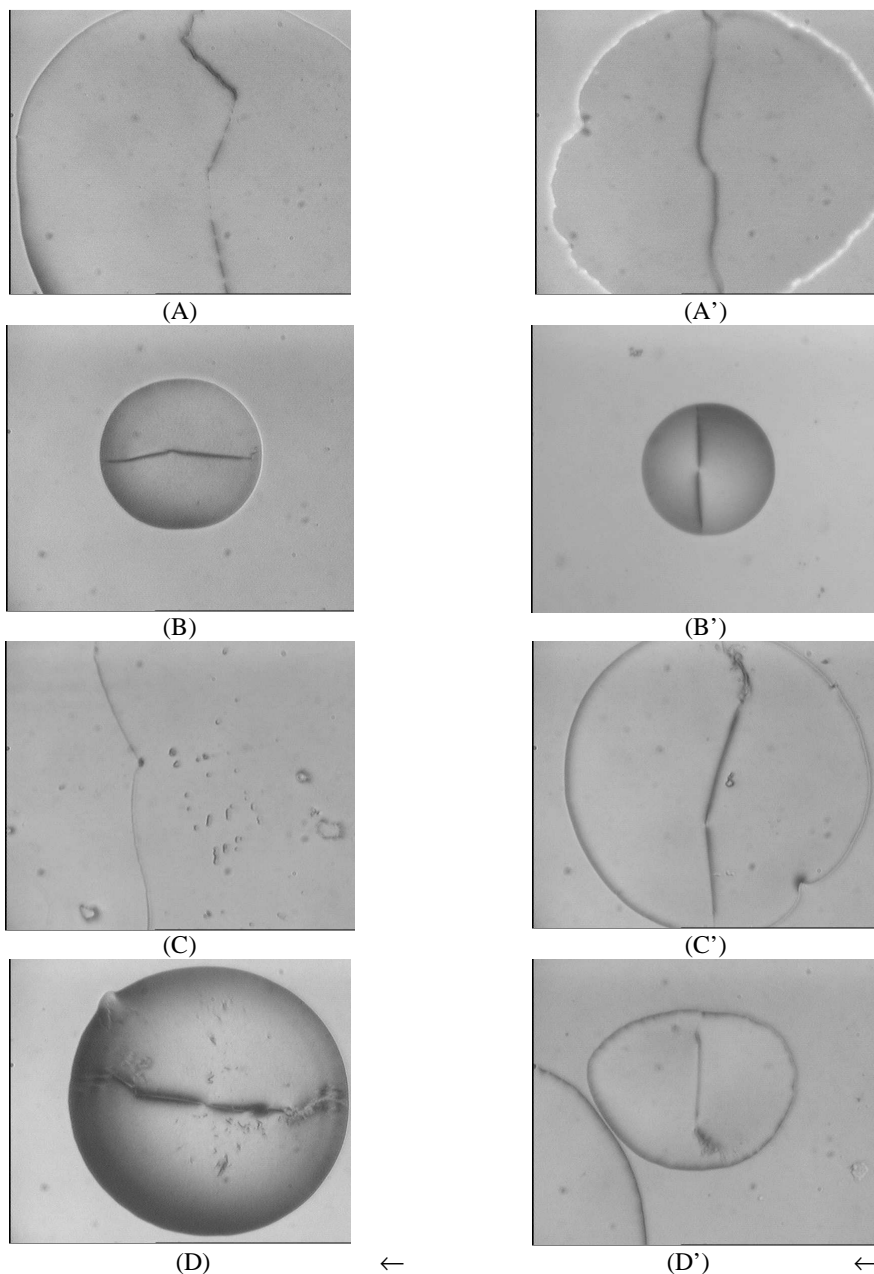


Fig. 2. Micrographs under polarized light of LC drops onto rubbed PVA (A, A', C, C') and PVI (B, B', D, D') substrate: LC5 (A, B), LC1 (A', B'), LC6 (C, D), LC4 (C', D'). Rubbing direction is indicated by the arrow.

As it was mentioned above, the mechanisms contributing to the LC alignment depend on the interactions between the LC molecules and the substrate. There are involved several types of such interactions: by van der Waals (orientation, induction and dispersion) forces, Coulomb interactions, quadrupolar forces, hydrogen bonding, π - π electron coupling, steric interactions, distortions of the orientation field of the LC due to the grooved or columnared surface etc. (e.g. [12-15]). The interaction type depends in turn on the structure of the LC and of the molecules in the alignment layer. Van der Waals forces between nonsymmetrical molecules have an orientational effect by

driving molecules into favorable mutual orientation, but this effect is rather small except for LCs and polymers where these forces can play an important role. In addition, van der Waals forces are particularly enhanced in interactions of LC molecules and polymer surface due to the nonadditivity property of these forces [16].

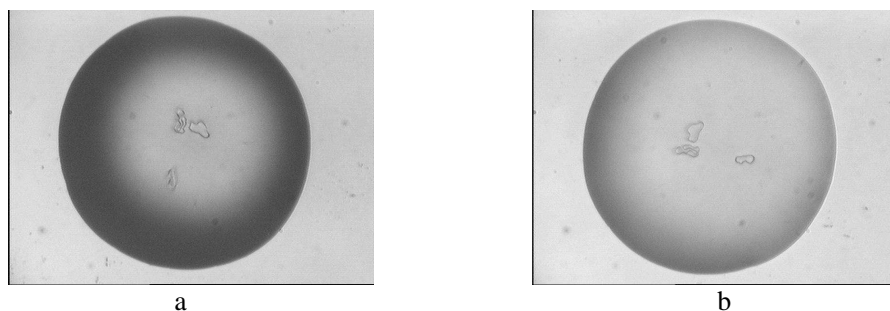


Fig. 3. Micrographs under polarized light of LC2 droplets onto rubbed PVA. Rubbing direction is the indicated by arrow and it is (A) parallel; (B) perpendicular to the direction of the polarizers.

Table 2. Summary of the observed alignment properties.

LC	Alignment layer	Alignment direction*
LC1	PVA	//
	PVI	//
LC2	PVA	//
	PVI	//
LC3	PVA	//
	PVI	//
LC4	PVA	//
	PVI	//
LC5	PVA	//
	PVI	⊥
LC6	PVA	//
	PVI	⊥
LC7	PVA	//
	PVI	⊥
LC8	PVA	//
	PVI	⊥

*Against the rubbing direction.

Additionally, it was found by polarized UV absorption spectroscopy and surface second-harmonic generation that the in-plane anisotropy of the LC adsorbed onto a polymer layer emerges only when LC molecules cover the whole surface and start to interact each other [17]. This fact shows that rubbed polymers give the orientation direction but interactions specific to the LC mesophases are also important for the alignment.

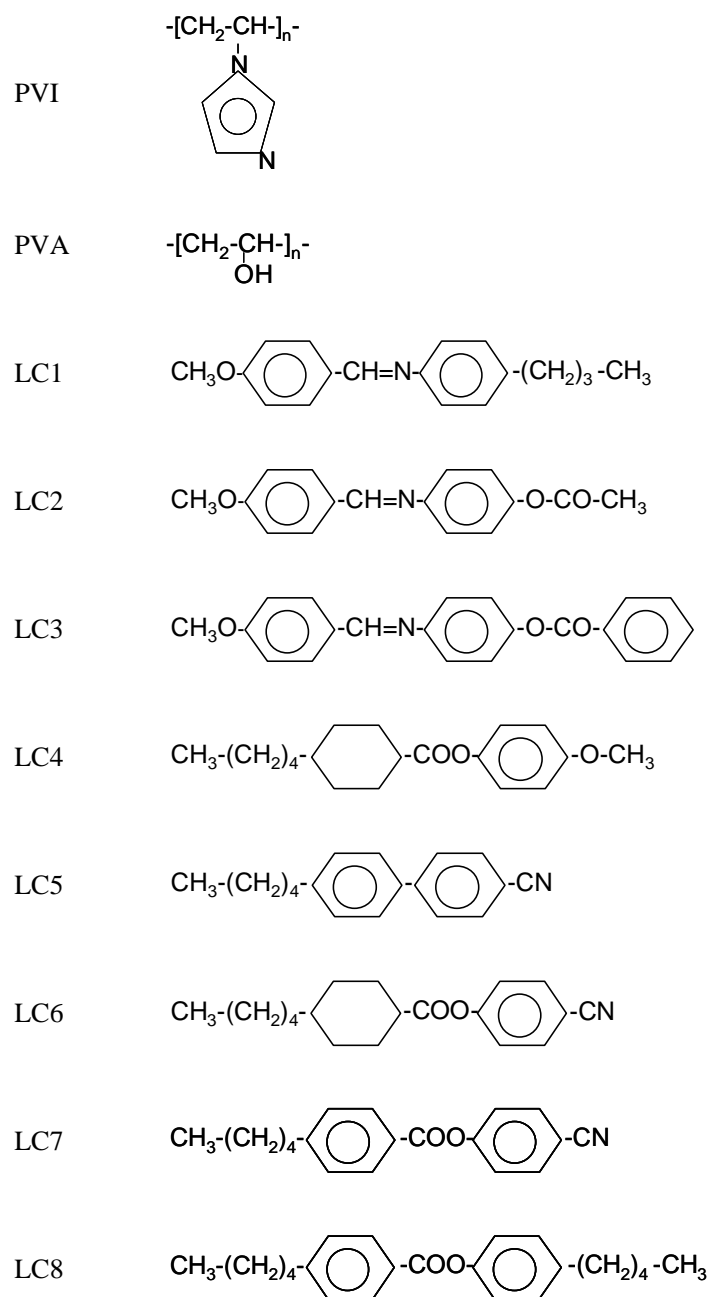


Fig. 4. Structure of the polymer substrates and of liquid crystals.

Molecular simulations performed for systems related to ours have shown that van der Waals interactions between the biphenyl core and the polyimide backbone are the most important type of interactions when cyanobiphenyl LC is parallel oriented onto polyimide, while in the case of a perpendicular orientation, the most important interactions are those between the end cyan groups and the carbonyl groups of the polyimide substrate [18]. In the case of a LC with a more complicate structure than cyanobiphenyl (e.g. an alkoxybiphenyl carboxylate), several factors contribute to the observed orientations: the natural tendency of the alkyl tails is to lie parallel to the polymer

backbone, while the (rigid) core prefers to straddle one or more polymer molecules [19]. Such a straddle over the polymer chains might also take place in our case of LCs containing carboxylate group: the alignment is then less imposed by the grooves.

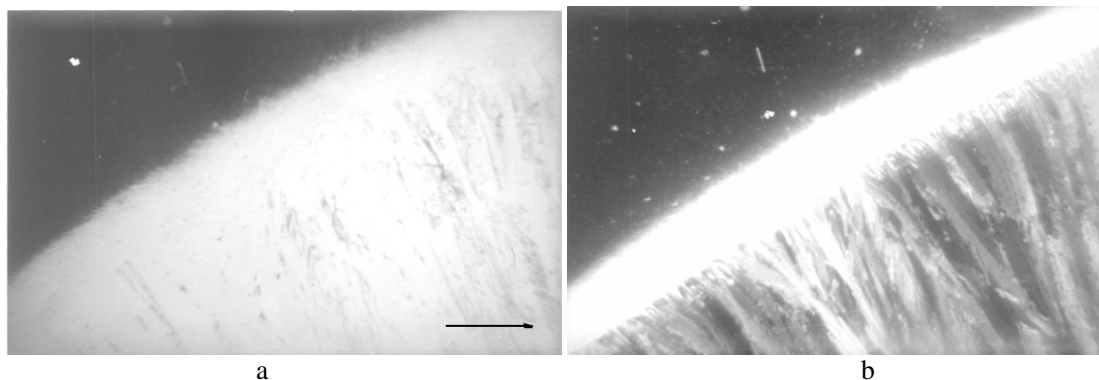


Fig. 5. Micrographs of a cell filled with LC4 (upper left corner) and LC6 (lower right corner) observed under crossed polarizers. The cell plates are prepared as mentioned in the experimental part. Arrow shows the rubbing direction. (A) Both LCs are in the nematic phase. (B) LC4 is in the nematic phase and LC6 is in the crystalline phase.

The structures corresponding to the components of the investigated systems are given in Fig. 4: One can see that there are cores more (LC1-LC3, LC5) or less (LC4, LC6) rigid and tail part(s) which are more (alkylate, cyan) or less (alkyl) polar or more (alkyl) or less (cyan) flexible.

More information on the interactions between the LCs and the PVI substrate was given from observing the cell features. Representative micrograph pictures of a cell having the plates covered with rubbed layers of PVA and PVI in antiparallel mounting and filled simultaneously with LC4 and LC6 are given in Fig. 5. LC4 is aligned parallel with the rubbing direction on PVA as well: Therefore, it appears dark between crossed polarizers. LC6 aligns parallel to the rubbing direction on PVA but perpendicular to this direction on PVI: Hence it appears light between crossed polarizers (part A). By cooling the cell (part B), LC6 (lower right corner) crystallizes first leading to its retraction. Between the dark region belonging to LC4 still in the nematic phase and the region occupied with crystallized LC6 there is a white region indicating a twisted structure. We supposed that this white region is occupied by LC4 after the retraction of LC6 by crystallization. However, the orientation of the LC4 molecules in this region is specific to LC6 molecules on the same substrates: this means that the orientation in this region might be given by an adsorbed layer of LC6 molecules remained after retraction by crystallization of LC6.

Let us comment more on the shown structures from the point of view of possible interactions. OH group in PVA has a dipole moment of ca. 1.7 D [20] with the major component parallel to the backbone, while the imidazole group in PVI is more polar (3.8 D [21]) the major component normal to the backbone. Therefore, rather big dipole moments are involved in the interaction between the alignment layer and the LC molecules. The LCs have either a positive or a negative anisotropy (Table 1) showing that the main component of the dipole moment is oriented either perpendicular to the long axis of the molecule or along this axis, respectively.

The structure of LC1, LC2 and LC3 differs only by one of the tails: it is respectively alkyl, acetate and benzoate. Since the alignment properties are similar on PVI and PVA, it might be concluded that the alignment properties are imposed by the core interactions with the substrate. However, this is not a general conclusion: the structure of LC4 and LC6 also differs only by the tail but they align similarly (parallel) on PVA but differently on PVI. The methoxy end-group seems to favor an orientation parallel to the rubbing direction on PVI. LC7 and LC8 have a core more flexible and less directed along the long molecular axis than in the case of biphenyl LCs. Their tails are cyan and alkyl, respectively. However, their alignment properties are similar each other and similar with those of the rode-like molecules of LC5.

In the case of sided polymers, both the main chains and the sided chains are ordered by rubbing [22]. PVI structure is related to the structure of polystyrene due to the presence of side aromatic rings. For that reason, we expect that PVI behaves similarly to polystyrene as concerning the alignment by rubbing; we suppose that its sided chains are mostly normal to the main chain and to the surface layer like in polystyrene rubbed layers.

The aromatic mesogens might interact anisotropically with the perpendicularly oriented phenyl rings via π - π interaction. However, the perpendicular alignment observed on the polystyrene layers [22] is less stable than that observed by us on PVI layer, showing that the interaction is weaker on polystyrene than on PVI film. Lee et al. [22] have speculated that the aliphatic tails of cyanobiphenyls might interact via van der Waals interactions with the parallel oriented vinyl backbone of polystyrene. Despite the existence of two alkyl end chains in LC8 molecule, the observed alignment on PVI is perpendicular to the rubbing direction, namely perpendicular to the vinyl backbone.

Further we focus the discussion on the alignment of LC4 and LC6. In the alignment of LC6 on rubbed PVI π - π interaction between phenyl ring and imidazole rings might prevail. The alignment of LC4 on rubbed PVI might be favored by the orientation of the moment dipole of sided imidazole ring as well as by van der Waals interaction between main chain of PVI and LC core. In the case of rubbed PVA, both permanent dipoles to the main chain and the major axis of the polarizability favor the parallel orientation of LC6.

Parallel alignment of LC4 on rubbed PVA is sought to be mainly given by van der Waals interactions.

The different alignment on the same rubbed polymer layer of two LCs differing only by one terminal group gives a measure of the complexity of the alignment mechanism of LC on substrates. Small changes in the structure of LC molecules modify the weights of different types of interactions in the total interaction energy and the prediction of the alignment of a certain LC on a given polymer substrate is a difficult task.

4. Conclusions

The orientational properties of polyvinyl imidazole rubbed films were investigated by observing the features of the liquid crystal droplets under the parallel polarizers using an optical microscope. Disclination lines passing through the droplet center were seen either parallel or perpendicular to the rubbing direction. The method was first time adapted to the case when the director is parallel to the LC/air interface, when a disclination line cannot be seen. Then, the droplet margins are investigated.

Rubbed films of polyvinyl imidazole present peculiar alignment properties for LCs, namely 5CB and three benzoates. These LCs are aligned perpendicular to the rubbing direction. The other investigated LCs are oriented parallel to the rubbing direction. Instead, all these LCs are oriented parallel to the rubbing direction on PVA films.

Three among the LCs which might be aligned perpendicularly to the rubbing direction have a cyan end-group, while the fourth has an alkyl tail. These groups seem to play a decisive role in the peculiar alignment properties.

It results that rather small changes in molecular structure of the LC leads to important changes in the balance of different contributions to the interaction energy. Consequently, quite different alignments might be obtained on PVI for related LCs.

Since the perpendicular alignment on PVI become parallel on PVA, the structure of the alignment layer is once more noticed.

Acknowledgements

The authors are indebted to Romanian Ministry of Education and Research (MEdC) for the financial support under Core Program 180.

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