Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Jego, C. , Leroux, N. , Agricole, B. and Mingotaud, C.(1996) 'Side-on liquid crystal polyacrylate in Langmuir-Blodgett films', Liquid Crystals, 20: 6, 691 — 696
To link to this Article: DOI: 10.1080/02678299608033161
URL: http://dx.doi.org/10.1080/02678299608033161

LIQUID CRYSTALS, 1996, VOL. 20, NO. 6, 691–696

Side-on liquid crystal polyacrylate in Langmuir–Blodgett films

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(*Received 28 July 1995; in final form 11 December 1995; accepted 19 December 1995*)

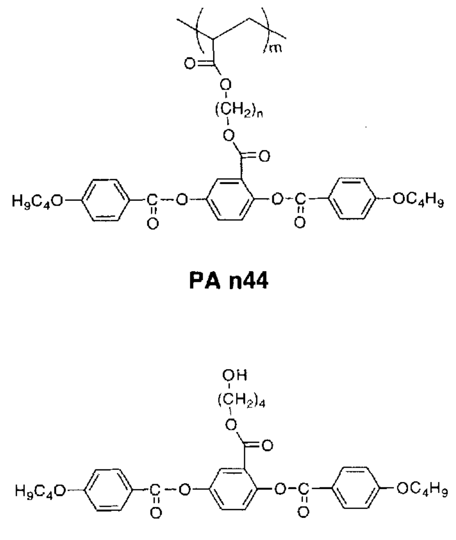
A side-on fixed liquid crystal polyacrylate has been investigated in Langmuir and Langmuir–Blodgett (LB) films. High in-plane orientation of the mesogenic groups has been observed within the LB multilayers, showing the ability of the LB technique to align a liquid crystal. The analysis of the in-plane order versus the dipping speed suggests some self-aggregation of the polymer in the monolayer. Within these aggregates, the molecular orientation (in-plane and out-plane) has been deduced from infrared dichroism experiments; the mesogenic group lies mainly parallel to the dipping direction and relatively flat on the substrate. This alignment of the polymer is however partially lost with time, leading to materials with less in-plane anisotropy.

1. Introduction

Alignment of liquid crystals has received much attention during the last decade. Electric or magnetic fields and surface treatment have been widely employed leading to a high degree of alignment of mesogenic compounds. Lately, Komitov *et al.* [1] have used Langmuir–Blodgett (LB) films of phosphatidylcholine derivatives in order to obtain a uniform homeotropic orientation of a nematic liquid crystal. Other authors using polyimide [2–4] or hemicyanine [5] LB films have succeeded in the alignment of nematic or smectic liquid crystals. This result clearly indicates that surfaces modified by the LB technique could be very useful in the liquid crystal field. However, it was thought until recently that the LB technique could not lead to planar alignment of molecules on a solid substrate; the built-up films are often considered as totally isotropic within the substrate plane. New experimental results seem to refute such a belief. Indeed, it has been shown for some specific monolayers that the built-up LB films do give molecular in-plane orientation. Such in-plane organization has been explained by flow orientation during the transfer process [6, 7]. Discotic compounds [8, 9], 'hairy rod' macromolecules [10, 11], phthalocyanines and related compounds [12, 13] lead to such an orientation process. This phenomenon offers the possibility of directly aligning the mesogens by the LB technique and not through the use of a modified surface. In the case of polymers bearing liquid crystal groups, very few reports [14] have been made concerning in-plane orientation. In this paper, we describe for the first time the behaviour of a side-on fixed liquid crystal polymer (see figure 1) which presents a very high in-plane orientation in LB films.

2. Synthesis and experimental

The side group precursor OH 444 and the PA *n*44 polymers were synthesized following established procedures [15–17]. Purification and analysis of PA *n*44 have been already described [17]. In particular, GPC analysis of the polymer gave the following parameters based


PA n44

OH 444

Figure 1. Molecular structures of compounds used in this work.

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upon polystyrene standard calibration:

PA 444 $\overline{\mathrm{M}_{\mathrm{w}}}=3000$, polydispersity $I=1{\cdot}7$, $\overline{\mathrm{DP}_n}=26$;

PA 644 $\overline{\mathrm{M}_{\mathrm{w}}}=34\,000$, polydispersity $I=1{\cdot}9$, $\overline{\mathrm{DP}_n}=30$.

Phase transition data for these polymers are reported in the table. Solutions of OH 444 molecule and the polymers (*c.* 1 mM per unit for the polymers) in chloroform (HPLC grade from Prolabo) were used as spreading solutions for the Langmuir film experiments.

A commercially available ATEMETA trough [18] equipped with a Wilhelmy balance was used for the Langmuir and Langmuir–Blodgett studies. Isotherms were obtained in the stepwise compression mode where the surface pressure Π is increased in steps usually of $2\,\mathrm{mN\,m^{-1}}$ with a waiting time of 15 to 30 min between successive compressions. Water used as the subphase for the Langmuir films was produced by a Millipore ultrapure water system with a specific resistance higher than $18\,\mathrm{M\Omega\,cm^{-1}}$. The monolayers were transferred onto $\mathrm{CaF_2}$ substrates for infrared studies. In the case of OH 444, the $\mathrm{CaF_2}$ substrates were precoated with 3 layers of behenic acid in order to ensure optimum transfer ratios. Typically 20 layers were transferred onto each substrate side.

Viscosity measurements were done using a KSV 5000 trough equipped with a channel lying between the two sides of the trough. Analysis of the results in terms of surface viscosity was done following reference [15].

IR experiments were conducted with a computer-controlled Nicolet 750 interferometer equipped with a KRS-5 metal grazing polarizer. IR spectra of the LB films were recorded quickly after the build-up of the material to avoid partial lost of the orientation with time (see below). The orientation of molecules in the LB films was determined by linear dichroism using infrared spectroscopy [19, 20]. The absorption of a polarized IR beam is proportional to $(\boldsymbol{\mu}_i\mathbf{E})^2$, where $\boldsymbol{\mu}_i$ is the transition dipole moment of the vibration being studied, and **E** is the local IR electric field. By changing the electric field orientation, it is possible to determine the orientation of $\boldsymbol{\mu}_i$. Using polarized light, one obtains three different IR spectra. In the first two cases, the incident light is parallel to the substrate normal while **E** is either parallel or perpendicular to the transfer direction **t**. In the third case, **E** is polarized parallel to **t**, whereas the IR beam is incident at an angle of 60° to the substrate normal. The in-plane and out-of-plane dichroic ratios α and β for each band are defined as: in-plane dichroic ratio $\alpha = A_{\perp}/A_{\parallel}$ and out-of-plane dichroic ratio $\beta(60^\circ) = A_{\parallel}(60^\circ)/A_{\parallel}(0^\circ)$, where A is the absorption of the IR band. The ratios α and β are related to the Euler angles ω and ϕ (see figure 2) describing the orientation of the transition dipole moment $\boldsymbol{\mu}_i$ through the following equations [20]:

$$P_2 = \langle \cos 2\omega \rangle = (1-\alpha)/(1+\alpha) \tag{1}$$

$$\langle \cos^2 \phi \rangle / \langle \sin^2 \phi \rangle = (1/2 + P_2/2)\cdot F(\beta, n_1, n_2, n_3, i, r) \tag{2}$$

where $\langle\rangle$ is the average over all possible orientations and F is a function depending on the refractive indices n_1 of air, n_2 of the LB film, and n_3 of the substrate. The refraction angle r is related to the angle i through the Snell–Descartes relation. Approximations made in deducing these equations are that the LB film thickness is small with respect to the IR wavelength, and that the IR absorptions are weak. The in-plane order parameter P_2 describes the average orientation of the transition dipoles within the plane of the film: $P_2=0$ for all dipoles having random distribution in the substrate plane; $P_2=1$ for all dipoles perfectly oriented in the transfer direction; $P_2=-1$ for all dipoles perfectly oriented in the direction perpendicular to the transfer. The molecular orientation with respect to the substrate (laboratory frame) can be deduced from the dichroic ratios of these IR absorptions together with equations (1) and (2).

Phase transition temperatures (in °C) for the PA *n*44 polymers: g = glassy state; N = nematic phase; I = isotropic liquid phase.

PA *n*44 polymers	g		N		I
$n=4$	●	40	●	116	
$n=6$	●	28	●	105	

3. Results and discussion

3.1. *Langmuir and Langmuir–Blodgett films*

The isotherms of OH 444 and PA 444 are given in figure 3. The monolayers of these compounds are highly

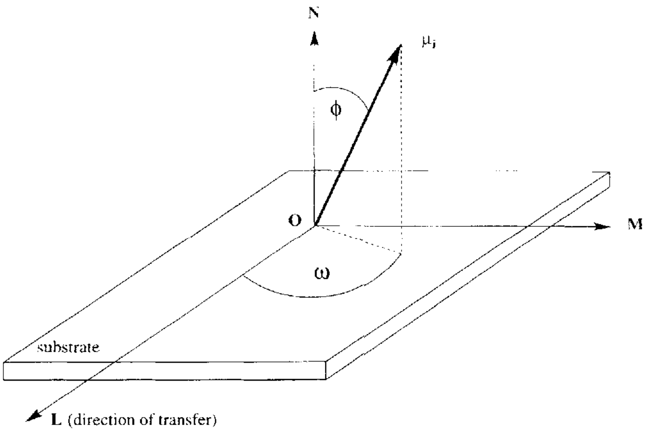

Figure 2. Angles ω and ϕ defining the orientation of a transition dipole moment $\boldsymbol{\mu}_i$ of the molecule with respect to the substrate system OLMN; the transfer direction **t** is parallel to the **L** axis.

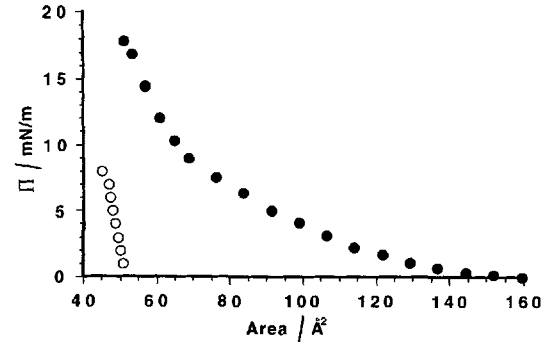

Figure 3. Compression isotherms of molecules of OH 444 (●) and PA 444 (○) at 20°C on pure water. The molecular area is per unit for the polymer.

stable with time. The onset of the OH 444 isotherm occurs at 160 $Å^2$, and collapse is observed at 18 mN/m for a molecular area close to 51 $Å^2$. In the case of the PA 444 polymer, a steeper isotherm is observed with a collapse area equal to 45 $Å^2$ per unit. Clearly, the polymer presents a more condensed phase than OH 444, even if the collapse areas of both compounds are similar. The small value for the collapse pressure of the PA 444 polymer indicates a smaller interaction of this polymer with the interface compared with OH 444. The isotherm of the analogue PA 644 (not shown) is similar to that of PA 444 within experimental error. This suggests that the length of the spacing methylene chain has no or little influence on the interfacial behaviour of such macromolecules.

The transfer onto hydrophobic solid substrates (CaF_2 plates precoated with three layers of behenic acid) could be done easily at 12 mN/m for the OH 444 molecules. Y type LB films are then obtained with a transfer ratio close to 0·9. Even if the surface pressure is small, LB films could be built up in the case of the polymers. For the PA 644 monolayer, the transfer was performed at 6 mN/m onto the hydrophilic substrate with a transfer ratio close to 0·7; Z type LB films were obtained. Surprisingly, PA 444 is much more difficult to transfer compared to PA 644 (the transfer ratio is very erratic). Because of this lack of reproducibility and the fact that stronger orienting properties (see below) are found for PA 644 compared with PA 444, we chose to focus our study on the PA 644 macromolecule.

3.2. *In-plane orientation in Langmuir–Blodgett films*

Polymer PA 644 presents clear in-plane orientation as demonstrated by the IR dichroism. Indeed, figure 4 shows that large differences in intensity can be found when the IR spectra are recorded with the light polarization set parallel or perpendicular to the dipping direction. Maximum in-plane dichroic ratios $1/\rho$ are found between 5 and 5·9 and correspond to order parameters close to 0·6–0·7. To our knowledge, these values are the highest reported for liquid crystal compounds oriented

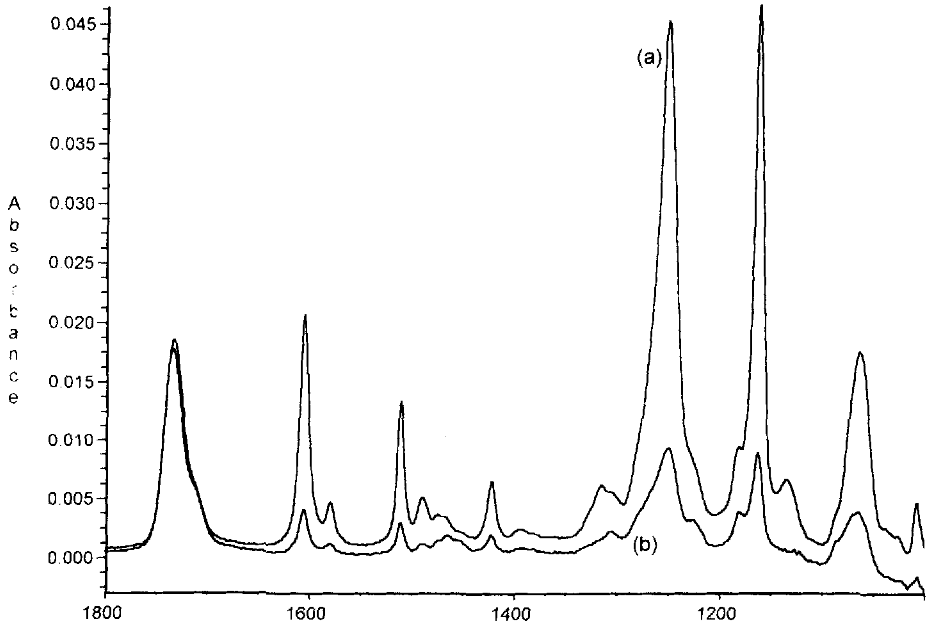

Figure 4. In-plane infrared dichroism of 20 layers of PA 644 deposited onto CaF_2 substrate with a dipping speed of 8 cm min^{-1}: (*a*) **E** parallel to the dipping direction; (*b*) **E** perpendicular to the dipping direction.

by the Langmuir–Blodgett technique and without annealing. This phenomenon of orientation, which induces here a planar alignment of the mesogenic units, has been explained by a flow orientation process occurring during deposition [7, 21]. Such an explanation supposed that the molecules or some aggregates of molecules having an elongated shape are oriented more or less parallel to the flow stream during the transfer of the Langmuir film onto the solid substrate. As demonstrated by various authors, this process depends mainly on the speed of deposition, the orientation being higher for a high speed of transfer. To verify this point in the case of PA 644 polymer, various depositions were done with different speeds. The order parameter (associated with the 1605 cm $^{-1}$ IR peak related to the main axis of the mesogenic core) is reported versus the dipping speed in figure 5. It increases quickly with the dipping speed and reaches a plateau corresponding to a maximum value of P_2. When the dipping speed is high enough, the orientation of the molecules or aggregates is then quasi-total and any increase of the speed does not change the order. This saturation in the ordering corresponds to the plateau in terms of order parameter. Before this plateau, the slope depends on various experimental factors as described by Minari *et al.* [6]. Indeed, the final equation obtained by those authors can be written in terms of the order parameter:

$$P_2/P_{2\max} = I_1(c)/I_0(c) \quad \text{with} \quad c = 2/\pi v_t/Da$$

where v_t is the dipping speed, P_2 is the in-plane order parameter measured for the corresponding dipping speed, $P_{2\max}$ is the maximum value of the order parameter (obtained for the highest dipping speed), D is the rotatory diffusion coefficient associated with the molecule or aggregates of molecules, a is the width of the substrate, and I_1 and I_0 are the modified Bessel functions of the zero'th and first order, respectively.

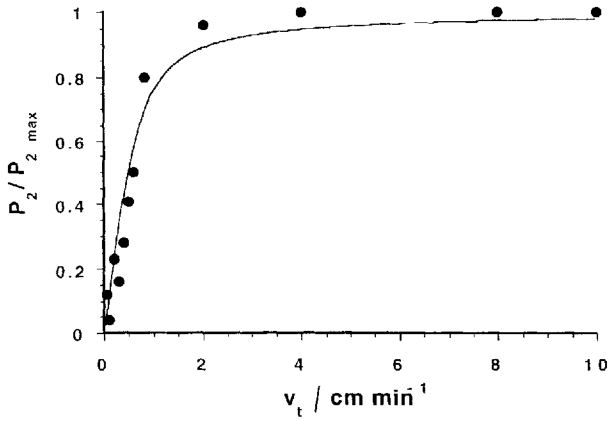

Figure 5. Dependence of the in-plane P_2 order parameter (associated with the 1605 cm $^{-1}$ IR peak) on the deposition speed v_t (cm min^{-1}). The solid line corresponds to the theoretical curve (see text).

The fit of the experimental points with the theoretical curve leads to a value of the rotatory diffusion coefficient, D. The theoretical curve obtained (see figure 5) indeed fits qualitatively the changes in order versus the dipping speed. However, the assumptions of this model, such as the monolayer being approximated to an ideal fluid and the trough regarded as infinite in its dimensions, are clear limitations for its application. The calculated value is certainly a rough estimation of the rotatory diffusion coefficient. At 20°C, one obtains $4 \pm 1 \times 10^{-3}\,\mathrm{s}^{-1}$ for the PA 644 film. This coefficient is theoretically related to the average shape and the average size of the moieties (molecules or molecular aggregates) which are oriented during the dipping process. Unfortunately, the shape anisotropy is unknown and exact calculation of the average size of the molecule or the aggregates is then impossible. According to Minari *et al.* [6], one can however estimate the order of magnitude of the length of the molecule or aggregates which are oriented by the flow during deposition. Indeed, the characteristic dimension L is linked to the rotatory diffusion coefficient through the relation:

$$D \approx kT/\eta L^2$$

where η is the surface viscosity of the monolayer.

In the case of PA 644, this surface viscosity is experimentally found to be $5{\cdot}4 \pm 0{\cdot}7 \times 10^{-2}$ sp at 20°C. The L dimension is then close to 140 nm. Taking into account the mean degree of polymerization of PA 644, the maximum length of the polymer in its totally extended conformation is less than 10 nm. The polymer length is then clearly too small to explain the order of magnitude of the rotatory diffusion coefficient, even if such a value is highly uncertain. This could indicate that it is not the polymer itself, but aggregates of PA 644 macromolecules that are oriented during the deposition of the LB film. The aggregation state of the polymer at the gas–water interface should depend on the temperature. Similar experiments were then carried out at 10°C for the same surface pressure. The calculated rotatory diffusion coefficient is similar ($3 \pm 1 \times 10^{-3}\,\mathrm{s}^{-1}$) even if the surface viscosity of the film increases to $0{\cdot}24 \pm 0{\cdot}04$ sp. This leads to a smaller value for the characteristic length of the aggregates of *c.* 60 nm for a maximum order parameter of about 0·6. These data seem to indicate an increase in the aggregation when the temperature increases. Similar results were observed with a Brewster Angle Microscope for triphenylene derivatives [8]. On the contrary, OH 444 does not present any in-plane orientation within the LB film, suggesting that the polymer backbone is needed for the aggregation process.

3.3. *Molecular orientation in Langmuir–Blodgett films*

When maximum in-plane orientation was achieved, more precise information on the molecular orientation was deduced from the IR dichroism experiments. For example, the IR bands in the 2800–3000 cm^{-1} region, associated with the stretching of CH bonds, present some in-plane dichroism (P_2 close to $-0{\cdot}2$). Since the transition dipole moment associated with the CH bond stretching is perpendicular to the hydrocarbon chain [22], this last result indicates that a part of the alkyl chains (i.e. polymer backbone, spacer and alkyl tails of the mesogenic groups) is oriented parallel to the dipping direction. However, the absolute value of P_2 is much lower than that associated with the mesogenic groups (see below). Because one expects the spacer chain to be mainly perpendicular to the mesogenic alkyl tails, such a result does not necessarily reflect disorganization of these chains within the LB film. On the contrary, the IR band at 1734 cm^{-1} presents no in-plane dichroism. On average, none of the CO bonds of the polymer present any preferential direction within the plane of the LB films. Peaks located at 1605 cm^{-1} and 1511 cm^{-1} are associated with CH vibrations of phenyl groups and correspond to a transition dipole more or less parallel to the mesogenic axis [23]. The orientation of these groups with respect to the dipping direction is then characterized by the P_2 parameter close to 0·7, proving that the long axis of the mesogenic core lies more or less parallel to the dipping direction. Similar orientations are found associated with the other IR peaks at 1422 cm^{-1}, 1250 cm^{-1}, 1163 cm^{-1} and 1065 cm^{-1}.

Out-of-plane dichroism of the 1605 and 1511 cm^{-1} peaks suggests that the long axis of the mesogenic group has a tilt angle close to 58° with respect to the normal to the substrate. A similar value is found for OH 444 (tilt angle close to 56°) indicating that this orientation is related to the molecular structure of the mesogenic group and not to the polymeric backbone.

The experiments conducted at 10°C lead again to very similar data; the out-of-plane tilt angle for the mesogenic group is still close to 56°. The main difference at this temperature is the size and the ordering of the PA 644 aggregates.

3.4. *Stability versus time*

The in-plane orientation of PA 644 LB films was analyzed as a function of time using the 1163 cm^{-1} IR peak. This one is indeed the strongest and enables an estimation of the polymer in-plane orientation with the highest accuracy. As shown in figure 6, a slight decrease of the in-plane orientation is observed at room temperature. After 50 days, the P_2 parameter loses 20% of its original value. When the sample temperature is slightly increased to 32°C, a temperature which is 4°C higher than the glass transition temperature T_g of PA 644, the loss of in-plane orientation is much faster (see figure 6). These differences with temperature can be easily understood in terms of a frozen molecular organization below T_g. The P_2 parameter seems however to reach a plateau associated with *c.* 20% of the original in-plane orientation. The origin of this plateau could be the first layers of polymers in contact with the substrate. Due to anchoring forces, these layers can lose their particular orientation only at much higher temperatures. In fact, total loss of in-plane orientation is indeed observed when the temperature is increased to 100°C.

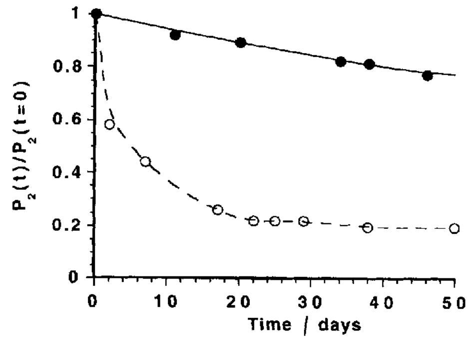

Figure 6. Typical decrease versus time of the in-plane order parameter (calculated for the IR 1163 cm^{-1} peak) of PA 644 LB films: at room temperature (●) and at 32 ± 2°C (○).

4. Conclusion

Planar alignment of a side-on fixed liquid crystal polymer was achieved by the Langmuir–Blodgett technique. Analysis of the in-plane orientation observed in the built-up films has suggested that some aggregation process occurs at the gas–water interface. The maximum in the in-plane order parameter (i.e. 0·6–0·7) describing the organization of mesogen units within LB films is obtained for high dipping speeds, when all aggregates are oriented by the stream flow induced by the dipping. The role of each part of the molecule on this aggregation process is still under study, even if the experiments herein described show that the polymer backbone is necessary for such self-aggregation. Further investigations are in progress to clarify the effect of anchoring forces on the LB stability.

The authors are indebted to Dr M. Mauzac for helpful discussions.

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