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Oriented polymer dispersed discotic liquid crystals

YANICK CHÉNARD, NADINE PAIEMENT and YUE ZHAO*

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec,
Canada J1K 2R1

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Polymer dispersed discotic liquid crystals (PDDLCs) were prepared using the hexa-*n*-octanoate of rufigalloi (RHO) and three polymer matrices: polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA). The molecular orientation of RHO in stretched PDDLC films was characterized by means of infrared dichroism. It was found that the stretching of films that contain RHO in both the columnar D1 and crystalline phase can effectively align columns of RHO along the stretching direction, with the short axes of the rigid cores lying in the plane of the film. By contrast with stretched polymer dispersed nematic liquid crystals, no orientation of RHO is induced for films stretched with RHO in the isotropic phase, followed by rapid cooling to room temperature. However, if stretched films are cooled under strain into the columnar D1 phase, orientation of RHO can develop with time.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) have been extensively studied because of their uses as electro-optical materials in many applications [1–3]. Much effort has been dedicated to various PDLC systems that contain nematic, cholesteric and smectic liquid crystals. To the best of our knowledge few, if any, studies were performed for polymer dispersed discotic liquid crystals (PDDLCs). Among the many features of PDLC which form the subjects of continuing studies, if a uniform LC orientation is obtained at the field-off state (in the absence of a voltage), interesting optical and electro-optical effects can be generated, allowing more applications to be envisaged. These include scattering polarizers based on oriented PDLC containing nematic LC [4, 5] and helical unwinding ferroelectric LC in sheared PDLC [6]. Recently, we have investigated orientation induction in mechanically stretched nematic PDLC films [7, 8]. The main finding is that, contrarily to liquid crystalline polymers that bear mesogenic side groups [9], it is hard to obtain a uniform LC orientation by stretching PDLC films with the LC compound in its LC phases. The LC anchoring at the polymer interface and the elastic deformations involved in the stretching of the LC droplets cause this difficulty. The key to achieving a uniform orientation is to have a LC that is phase-separated from the polymer matrix in the liquid state ($T > T_{NI}$: the nematic–isotropic transition temperature).

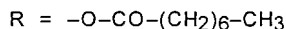
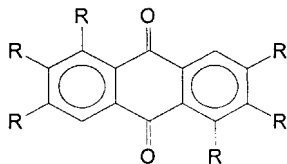
When PDLC films are stretched with the LC compound in the isotropic phase, its liquid droplets can easily be deformed. A subsequent cooling of the stretched film under strain leads to a uniform LC orientation along the long axes of the droplets. This orientation induction occurs when molecules inside the elliptical droplets form the nematic phase. In the case of a PDLC composed of 4-octyl-4'-cyanobiphenyl (8CB) and polyacrylic acid (PAA) [7], a uniform orientation was achieved under film extensions as small as 20%. Parallel LC anchoring at the polymer interface in this system favours the LC orientation along the long axes of the droplets. Nevertheless, a uniform orientation was also obtained for a system made from PAA and a nematic mixture BL006, in which a perpendicular LC anchoring is revealed by the radial configuration of the spherical LC droplets in non-stretched films [8].

As a result of these observations, it is of interest to investigate orientation induction for a PDDLC with a discotic LC displaying columnar mesophases. For PDDLCs in general, it is valuable to study the phase separation of a discotic LC in mixtures with polymers, as well as the effects of the resulting morphologies and confined geometries on the columnar phases. For the LC orientation in particular, one would like to know (a) how the molecules or columns could be oriented through a mechanical stretching, (b) the conditions leading to a uniform molecular orientation, and (c) the role played by anchoring effects as compared with systems containing nematic LC. In this paper, we report an investigation on a PDDLC, which is part of our studies on oriented PDLCs using infrared dichroism.

* Author for correspondence
e-mail: yzhao@courrier.usherb.ca

2. Experimental

The discotic LC used in this study was the hexa-*n*-octanoate of rufigallol (RHO). The sample was prepared using a reported method [10]. The chemical structure and the polymorphism of RHO, as determined by differential scanning calorimetry (DSC) (heating and cooling rates: $10^{\circ}\text{C min}^{-1}$) are shown below.



Heating: crystalline $\xrightarrow{111^{\circ}\text{C}}$ columnar D1 $\xrightarrow{131^{\circ}\text{C}}$ isotropic liquid
 Cooling: isotropic liquid $\xrightarrow{127^{\circ}\text{C}}$ columnar D1 $\xrightarrow{89^{\circ}\text{C}}$ columnar D2 $\xrightarrow{63^{\circ}\text{C}}$ crystalline

RHO has two columnar mesophases: D1 is an enantiotropic phase and D2 is monotropic. It has been reported [11] that both columnar phases have a two-dimensional rectangular lattice but differ in the size of the lattice and molecular orientations in the columns. Previous work on RHO in this laboratory has investigated its crystallization kinetics from the two columnar phases [12] and its phase transitions when confined into porous membranes [13].

Films of PDDLC were prepared by dissolving RHO and the polymer matrix in tetrahydrofuran (THF) and casting the homogeneous solution onto the surface of a glass plate. After evaporation of most of the solvent at room temperature, the films were further dried in a vacuum oven at 80°C for two days. The polymers used were poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and polystyrene (PS). The concentration of RHO was 30 wt %. The three polymer matrices were chosen because their mixtures with RHO showed phase separation and their films could be stretched within a range of temperatures which covers the crystalline, D1 and isotropic phases of RHO. Phase separation in the films of all three systems was induced by solvent evaporation. Before each experiment, the film used was heated to 140°C , in the isotropic phase, for equilibrium. It was found that even at this or higher temperatures, RHO remains phase-separated from the polymer. For film stretching, the film was placed inside a temperature-controlled stretching device and heated from ambient to a pre-determined stretching temperature; then the stretching was carried out at a rate of about 20 mm min^{-1} . The film extension was measured in terms of the draw ratio λ , which is defined as the ratio of the film length after stretching over that before stretching. Unless otherwise stated, immediately after stretching the film was cooled rapidly, under strain, to room temperature for

the orientation measurement. Infrared dichroism was used to characterize the average orientation of the RHO molecules through the determination of the order parameter. Details of the use of this infrared technique to study oriented PDLC films were reported elsewhere [7, 8]. Polarized infrared spectra were recorded on a Bomem MB-102 FTIR spectrometer. A wire grid polarizer was placed between the sample and the DTGS detector of the spectrometer. Phase transitions of RHO in the films were measured using a Perkin-Elmer DSC-7 apparatus and a Leitz DMR-P polarizing microscope equipped with an Instec hot stage.

3. Results

RHO has a low solubility limit in the three polymers used. The strong phase separation can easily be seen from DSC and microscopic observations. Figure 1 shows the DSC heating curves of the three systems containing 30% of RHO and also pure RHO for comparison. Overall, the low solubility of RHO is reflected by the slight changes in the transition temperatures of crystal-to-D1 ($T_{\text{Cr-D1}}$) and D1-to-isotropic liquid ($T_{\text{D1-I}}$) for RHO and in the T_g s of the polymers. As compared with pure RHO, $T_{\text{Cr-D1}}$ is depressed by only a few degrees in these PDDLCs. The effect on the columnar D1 phase is relatively stronger, particularly in the matrix of PS, where the temperature range of the D1 phase is narrowed by about 10°C . The DSC measurements also provide the basis for performing mechanical stretching of the films, since they can be deformed only at temperatures above T_g of the polymer matrix. In the case of PS/RHO, T_g is at about 83°C . Therefore, the films can be stretched at temperatures with RHO in all the three phases: crystalline, D1 and isotropic liquid. This, in principle, is also the case for PEMA/RHO whose T_g is at 72°C . However, because of the low T_g , the films were stretchable only with RHO in the crystalline phase; they were

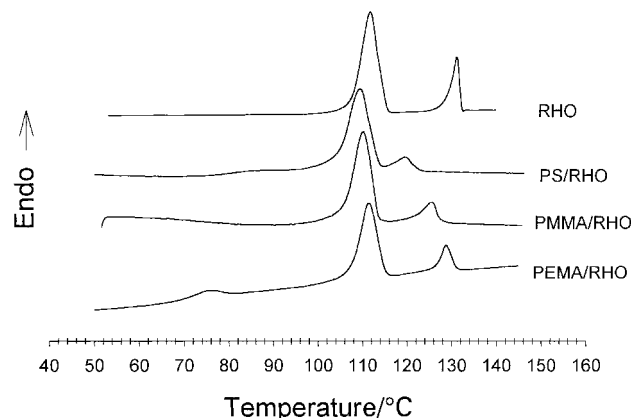


Figure 1. DSC heating curves for PS/RHO, PMMA/RHO, PEMA/RHO and pure RHO.

broken when stretched at higher temperatures. In order to stretch PDDLC having a polymethacrylate matrix with RHO in the D1 and isotropic phase, films of PMMA/RHO were used. The T_g of the matrix should be around 105°C; it cannot be seen because of overlap with the crystal melting endotherm of RHO.

The three systems display different morphologies resulting from phase separation. To show this, a set of phase-contrast and polarizing micrographs is presented in figure 2. For all samples, the phase-contrast micrograph was taken at 140°C where RHO is in the isotropic phase. Two phases are visible, indicating phase separation in the isotropic phase. In PS, RHO forms spherical droplets embedded in the polymer matrix, which is similar to nematic LC in PDLC. By contrast, in both PEMA and PMMA, spherical droplets are absent. Instead, irregular domains appear, which is generally indicative of two continuous phases. The domains are larger in PEMA than in PMMA. These differences in morphology are also observable on the polarizing micrographs taken at ~115°C with RHO in the D1 phase. Large domains of the phase rich in RHO allow LC textures to develop,

particularly for PEMA/RHO, where textures characteristic of the columnar phase can be seen. In PS, however, only birefringent spots can be seen. Qualitatively, these microscopic observations are consistent with the DSC results shown in figure 1. Among the three matrices, the strongest confinement of RHO in PS, as revealed by the morphology, explains the strongest effect on the phase transitions of RHO. For the two polymethacrylates, the smaller phase-separated domains in PMMA implies stronger interaction between molecules of RHO and the matrix, resulting in greater effects on the columnar D1 phase.

To explain the use of infrared dichroism, figure 3 gives examples of polarized infrared spectra for (a) a film of PS/RHO prior to stretching, (b) the PS/RHO film stretched at 100°C to $\lambda = 2.5$, and (c) a film of PMMA/RHO stretched at 115°C to $\lambda = 2$ (the PEMA/RHO system has similar spectral features). The spectra were recorded at room temperature with the infrared beam polarized parallel and perpendicular to the film stretching direction. For the unstretched film, figure 3(a), no infrared dichroism can be seen indicating the absence of

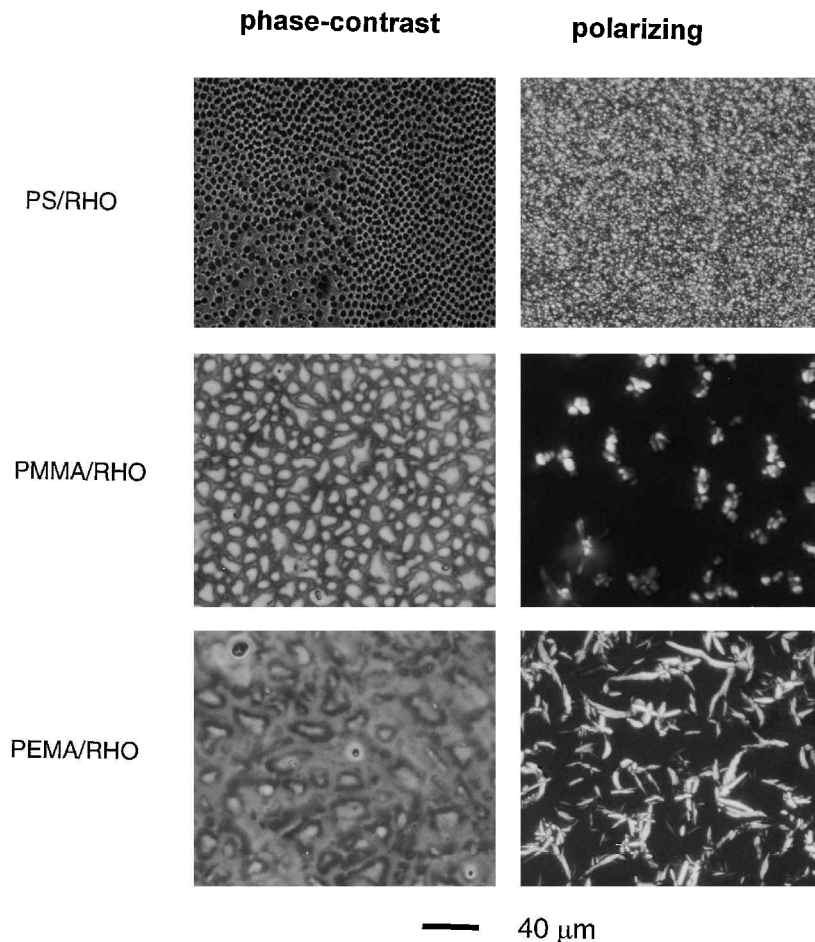


Figure 2. Phase-contrast optical micrographs taken in the isotropic phase, and polarizing micrographs taken in the D1 phase for films of PS/RHO, PMMA/RHO and PEMA/RHO.

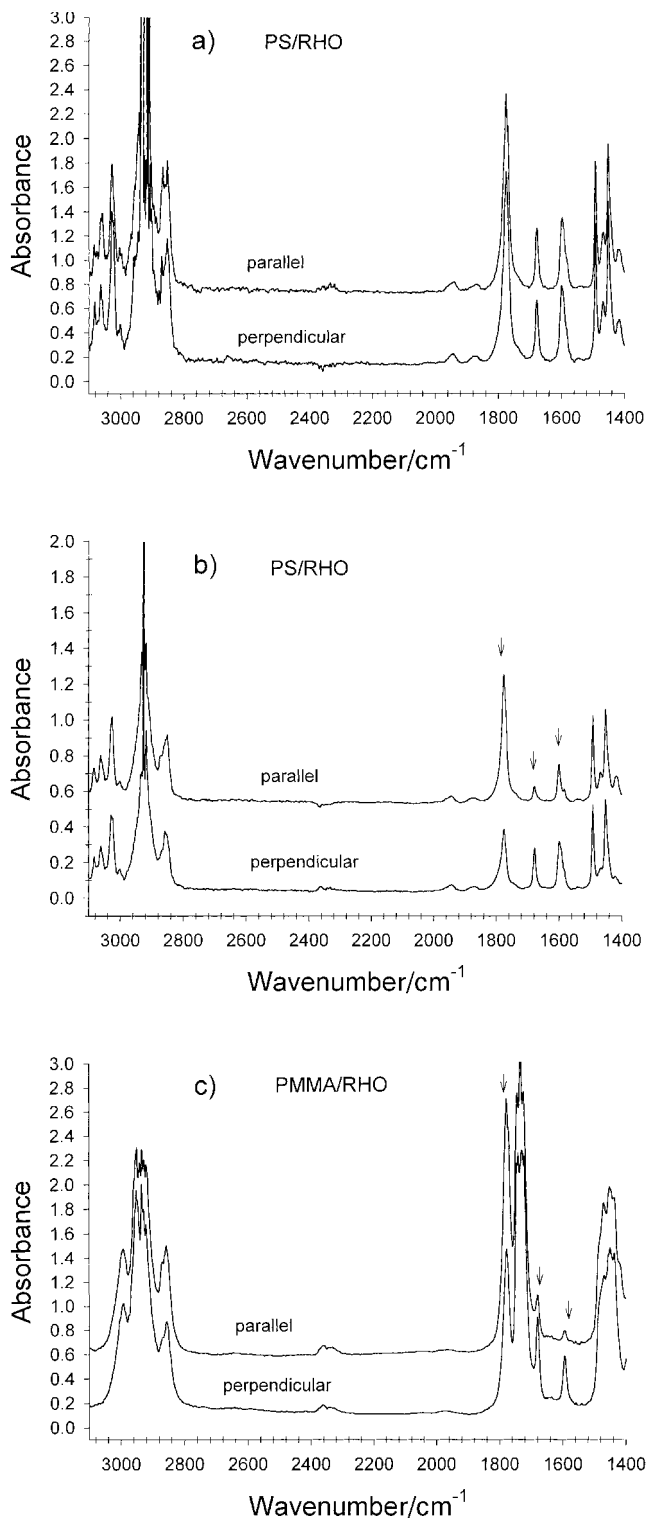


Figure 3. Polarized infrared spectra taken at room temperature for films of (a) PS/RHO prior to the stretching, (b) PS/RHO stretched at 100°C to $\lambda=2.5$ and (c) PMMA/RHO stretched at 115°C to $\lambda=2$. The two spectra in each figure were recorded with the infrared beam polarized parallel and perpendicular to the stretching direction.

any preferred molecular orientation in the sample. The same result was observed for all unstretched films regardless of the polymer matrix. The situation is different for the stretched films. In the case of PS/RHO, figure 3(b), the well isolated band at 1678 cm^{-1} is assigned to the two C=O groups of the rigid core of rufigallol. Defining the short axis of the core as the line connecting the two C=O groups, the strong perpendicular dichroism of this band indicates that the short axes of the rigid cores are aligned perpendicular to the stretching direction. Thus, for PS/RHO, the order parameter S was determined from $S = (A_{\parallel}/A_{\perp} - 1)/(A_{\parallel}/A_{\perp} + 2)$, using the polarized absorbances A_{\parallel} and A_{\perp} of the 1678 cm^{-1} band. It should be emphasized that, by definition of the order parameter, S measures the orientation averaged over all short axes of the rigid cores. The band at 1776 cm^{-1} arises from the six C=O groups that link the rigid core and the flexible alkyl chains of RHO. This band, showing a parallel dichroism, was not used to determine S , as the angle between the transition moment and the short axis was unknown. Other bands of RHO, such as the one at 1600 cm^{-1} assigned to the C–C aromatic stretching vibration and those related to the CH₂ and CH₃ groups in the region of 2800–3000 cm^{-1} , are overlapped with the bands of PS; quantitative measurement could not be made from those bands.

For the stretched films of PMMA/RHO and PEMA/RHO, the use of the infrared bands is different. As can be seen from the example in figure 3(c), the polymethacrylate matrix has a strong C=O band around 1730 cm^{-1} which overlaps with the various C=O bands of RHO at 1776 and 1678 cm^{-1} . However, the phenyl band of RHO at 1594 cm^{-1} is now clear and well suited to the calculation of the order parameter. As the transition moment of this band is also parallel to the short axis of the rigid core, the same equation of $S = (A_{\parallel}/A_{\perp} - 1)/(A_{\parallel}/A_{\perp} + 2)$ was utilized. For this stretched PMMA/RHO film, again, the strong perpendicular dichroism of the 1594 cm^{-1} band, like the 1678 cm^{-1} band, indicates a perpendicular orientation of the short axes of the rufigallol cores. To summarize, in the following the order parameter refers to the average orientation of the short axes of the rigid cores of RHO in stretched PDDLC films. On the basis of these data, we discuss the alignment of molecules and columns.

Figures 4–6 show the results of order parameters measurement at room temperature on films stretched at different temperatures to various draw ratios for the three systems. Three stretching temperatures were used for PS/RHO (figure 4), with RHO in the crystalline, D1 and isotropic phase. Only one stretching temperature was used in the case of PEMA/RHO (figure 5), whose films can only be stretched with RHO in the crystalline

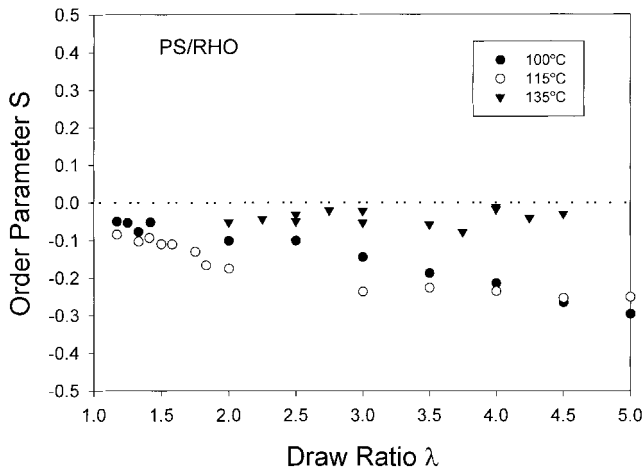


Figure 4. Order parameter measured at room temperature vs. draw ratio for PS/RHO films stretched at 100°C (crystalline phase), 115°C (D1 phase) and 135°C (isotropic phase).

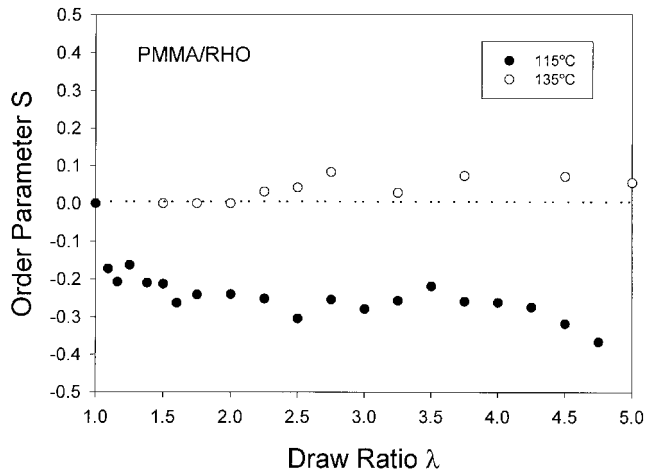


Figure 6. Order parameter measured at room temperature vs. draw ratio for PMMA/RHO films stretched at 115°C (D1 phase) and 135°C (isotropic phase).

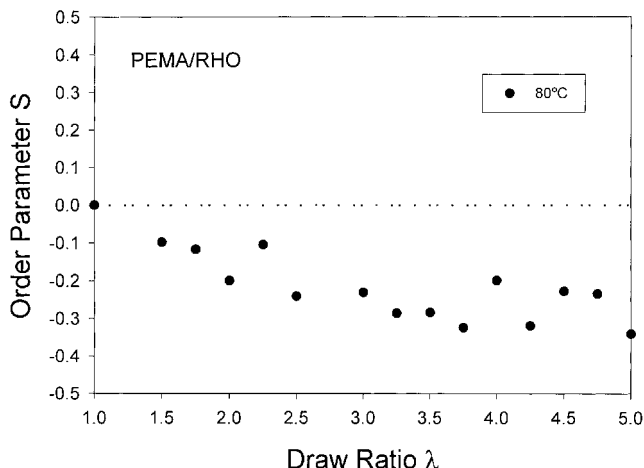


Figure 5. Order parameter measured at room temperature vs. draw ratio for PEMA/RHO films stretched at 80°C (crystalline phase).

phase. Two stretching temperatures are shown for PMMA/RHO (figure 6) which, contrarily to PEMA/RHO, can be stretched only with RHO in the D1 or isotropic phase. Examining the whole of the results, several features emerge. First, a macroscopic orientation of the rigid cores of RHO is achieved by stretching films with RHO in the crystalline or D1 phase; the rigid cores are aligned with their short axes perpendicular to the stretching direction (negative values for the order parameter). Secondly, closer inspection indicates that, upon film extension the orientation development is faster for films stretched in the D1 phase than in the crystalline phase of RHO; at high draw ratios the orientation level is similar. Thirdly, when the films are stretched with RHO in the isotropic phase, the orientation obtained is negligible within experimental error. Similar results were obtained when different

stretching temperatures were used for RHO in the same phase. An example is shown in figure 7, where the order parameter at a fixed $\lambda = 2.5$ is plotted as a function of stretching temperature for films of PMMA/RHO. It is seen that an almost constant orientation is obtained for stretching in the D1 phase, whereas the orientation drops to near zero once the stretching is performed beyond the D1-to-isotropic transition temperature.

4. Discussion

The first question is how the columns of RHO are organized in the stretched film to give rise to the observed molecular orientation. The sketch in figure 8 illustrates the two possibilities. In (a), the columns are

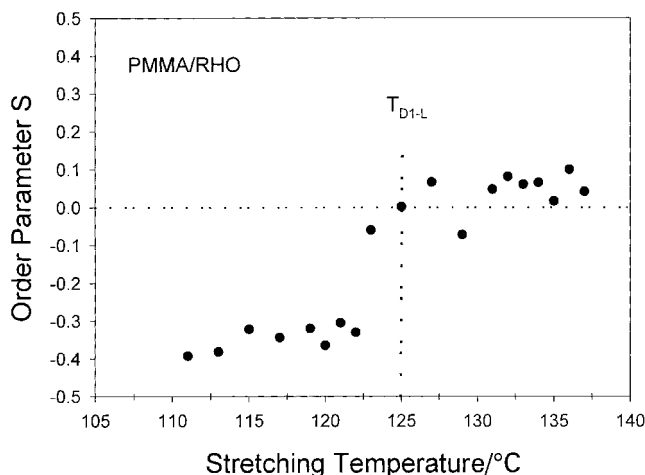


Figure 7. Order parameter measured at room temperature vs. stretching temperature for films of PMMA/RHO stretched to $\lambda = 2.5$. The D1-to-isotropic phase transition temperature is indicated.

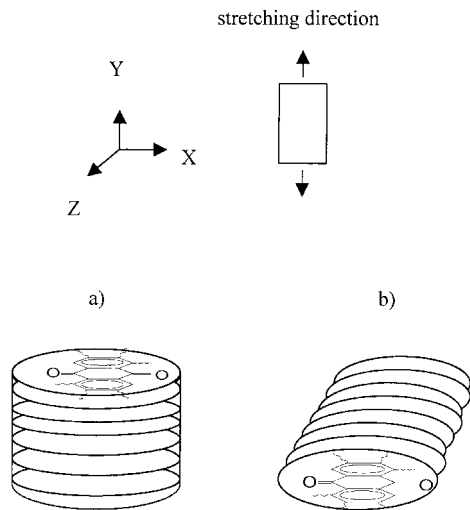


Figure 8. Schematic illustration for column alignment options in stretched films, which can lead to the observed perpendicular orientation of the short axes of the rigid cores (the line connecting the two C=O units) with respect to the strain direction.

aligned in the stretching direction, with the short axes of the rigid cores lying in the plane of the film (plane XY), while the long axes point out of the film surface. The second possibility, as shown in (b), is to have the columns aligned in the direction normal to the film surface; both axes of the rigid cores stay in the plane of the film and the short axes are perpendicular to the strain direction. These two situations can lead to the infrared data shown in figures 4–7. Generally, when discotic liquid crystals are confined between two parallel surfaces, they adopt one of two basic configurations [14]: the plane of the rigid core is parallel to the surface ('side-on') or the plane normal is parallel to the surface ('edge-on'). For stretched PDLC or PDDLC films, LC molecules are confined inside elliptical or cylindrical domains that have a curved interface with the polymer matrix. It is reasonable to believe that an alignment of the columns in the stretching direction, i.e. along the long axes of cylindrical domains, is most probable, corresponding to the 'edge-on' situation for the RHO molecules. There is no particular reason to suggest the alignment of columns normal to the film surface, i.e. perpendicular to the long axes of elongated domains. Such a situation would mean, for the same RHO molecules, 'side-on' with respect to a portion of the interface and 'edge-on' for the rest. On the other hand, the columns, which should react as entities to the stretching, are likely to align their long axes in the stretching direction. On the basis of the above analysis, the results suggest that the columns of RHO are aligned in the stretching direction while the short axes of the rigid cores lie preferentially in the plane of the film. No infrared dichroism should be observed if the short axes

are randomly oriented in the plane perpendicular to the stretching direction (plane XZ), even under a perfect alignment of the columns.

Another observation in this study, which is quite surprising, is the effective orientation induction for films stretched with RHO in the crystalline phase. One would expect to see little, if any, macroscopic orientation induced since the crystalline phase should lose the fluidity that is characteristic of LC phases. Therefore, the results imply that the alkyl chains of RHO could still possess mobility in the crystalline phase, which is responsible for the deformability of crystalline RHO. In other words, in these PDDLC systems, it is possible that the crystalline structure of RHO does not include completely ordered alkyl chains. This may be true at least for those alkyl chains in contact and interacting with the polymer interface, which ensures the transfer of the mechanical stress and the deformation of the droplets or domains of crystalline RHO. In this way, the columns formed by the rigid cores, and surrounded by the mobile alkyl chains, can be aligned as entities along the stretching direction. The important difference in order and structure between the rigid cores and mobile alkyl chains is also reflected by the absence of a significant orientation of the latter in stretched films. As is seen in figure 3, the infrared bands in the $2800\text{--}3000\text{ cm}^{-1}$ region, which should mainly arise from the alkyl chains of RHO (each RHO molecule has 36 CH_2 and 6 CH_3 units), shows no noticeable dichroism (the CH_2 symmetrical stretching vibration around 2860 cm^{-1} , for example).

The results of this study appear to contrast sharply with what was observed for PDLC containing nematic LC [7, 8]. As outlined in the Introduction, the effective way to induce the LC orientation for nematic PDLC is to stretch films with the LC compound in the isotropic phase, while direct stretching of nematic droplets results in lower orientation due to anchoring effects. The results shown in figures 4–7 seem to indicate the opposite for PDDLC made from RHO. Considering that molecules of nematic LC inside elongated droplets are aligned rapidly once they enter the nematic phase during cooling, the question for discotic LC is whether the alignment of columns could take more time to develop inside elongated domains. In fact, all the three systems have a narrow temperature range for the D1 phase (figure 1).

When a film is stretched in the isotropic phase and then removed from the oven to room temperature, it does not take long for the film to cool into the crystalline phase, where the molecular mobility is reduced. Therefore, it is possible that the apparent incapacity to develop column alignment inside elongated domains, following the isotropic phase stretching, is caused by a kinetic factor. The following experiment has been performed for both PS/RHO and PMMA/RHO in order to check this

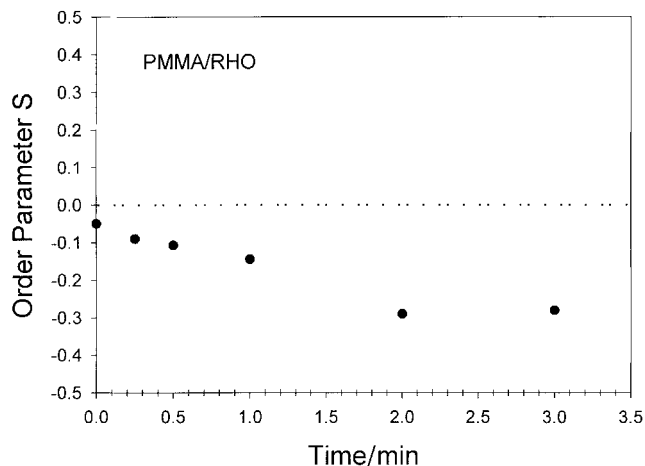


Figure 9. Order parameter measured at room temperature vs. the time for a PMMA/RHO film to be retained under strain at 115°C (D1 phase). The film was stretched in the isotropic phase at 135°C to $\lambda = 3$ before being cooled into the D1 phase.

possibility. After the film was stretched in the isotropic phase, instead of removing it out of the oven for fast cooling, the film was cooled into the D1 phase and remained there for some time before cooling to room temperature for the orientation measurement. For both systems, orientation of RHO was indeed observed after this treatment. An example of the results is shown in figure 9 for PMMA/RHO, where the order parameter measured at room temperature is plotted as a function of the time for the film to be retained at 115°C (in the D1 phase) after being stretched at 135°C to $\lambda = 3$. Each point in this figure corresponds to a separate experiment on a new sample. It is seen that when cooled from the isotropic phase column alignment can develop in the columnar D1 phase. It takes about 2 min to achieve an orientation level similar to that obtained by direct stretching in the D1 phase (figure 6). Therefore, similar to nematic LC, orientation of discotic RHO can be achieved from molecules undergoing the isotropic-to-D1 phase transition inside elongated domains. But the

results suggest that it takes a longer time for the alignment of columns than for the orientation of nematic molecules. For these PDDLc, more studies are needed to understand the strength and natures of anchoring as well as effects on the alignment of columns of RHO. For instance, strong 'edge-on' for RHO molecules in the D1 phase should favour the alignment of columns after an isotropic phase stretching and cooling under strain.

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