Macromolecules **1996,** *29,* 4619−4625

Mechanically-Induced Alignment of Mesophases

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Received November 7, 1995; Revised Manuscript Received March 13, 1996[⊗]

ABSTRACT: We report the results of a systematic orientation study on side-chain liquid crystalline polymers (SCLCPs) mechanically stretched in different mesophases. Two representative polyacrylate-based SCLCPs were used. The study demonstrates that the macroscopic orientation of the mesogens reflects a direct alignment of the liquid crystalline domains as entities under the effect of a mechanical field. One important feature is that the alignment of different mesophases results in different orientation directions of the mesogens with respect to the mechanical stretching direction. On the basis of our results, it seems to be common that stretching SCLCPs in their smectic phase gives rise to a macroscopic orientation perpendicular to the stretching direction. When SCLCPs are stretched in a nematic phase covering a wide temperature range, this orientation is achieved along the stretching direction. However, a perpendicular orientation can also be induced when SCLCPs are stretched in a nematic phase which is only over a narrow temperature range (ca. 10 °C or fewer) beyond a smectic phase. A sharp inversion of the orientation direction often occurs when SCLCPs are stretched in the mesophase transition regions. We show that the observed alignment behavior of the different mesophases could be explained by assuming an alignment, always along the stretching direction, of the long axes of liquid crystalline domains.

Introduction

One way to induce a macroscopic orientation of the mesogens in side-chain liquid crystalline polymers (SCLCPs) is to perform a mechanical stretching. Among the rich orientation behavior displayed by SCLCPs, one intriguing phenomenon is that the macroscopic orientation can develop either along with or perpendicularly with respect to the stretching direction. The perpendicular orientation was seen on smectic SCLCPs,[1] on nematic SCLCPs having an odd number of CH_2 units in the flexible spacer which links mesogen and chain backbone,[2] and also on nematic SCLCPs containing six CH_2 units in the spacer.[3] This phenomenon has not been clearly understood yet, partly due to the lack of systematic investigations on SCLCPs exhibiting different mesophases.

As part of the effort for understanding the mechanically-induced orientation of SCLCPs, we have recently proposed a mechanism[4] which could account for a wide range of observations and be corroborated by many experimental results reported in the literature. Instead of emphasizing a response of the mesogenic side groups to the alignment of the chain backbone by virtue of a hinge effect imposed on these two constituents through the spacer,[5] the mechanism is focused on a direct response of the intrinsically oriented microstructure, i.e., the nematic domains or smectic layers, to the mechanical field. The key point is the suggestion that the observed macroscopic orientation of the mesogens be mainly related to a direct alignment of the mesophases. The liquid crystalline domains could be anisotropic in shape and, owing to the intermolecular cooperativity, respond to a stretching force as entities by aligning their long axes along the stretching direction. Consequently, the macroscopic orientation direction of the mesogens is determined by the orientation of the mesogens relative to the long axes of the liquid crystalline domains before the stretching-induced alignment. As schematically depicted in Figure 1, three basic situations can be envisaged. In (a), a smectic-A layer is shown. It is likely that the plane's normal, which is the orientation direction of the mesogens, is perpendicular to the domain's long axis. A perpendicular macroscopic orientation of the mesogens should be observed after the alignment of the smectic layers by the action of a mechanical field. In (b), it is conceivable to expect nematic domains whose directors are also perpendicular to the domains' long axes, and a mechanical stretching should still result in a perpendicular macroscopic orientation. Finally, in (c), the director of the nematic domain coincides with the domain's long axis, and the stretching should give rise to a macroscopic orientation of the mesogens parallel to the stretching direction.

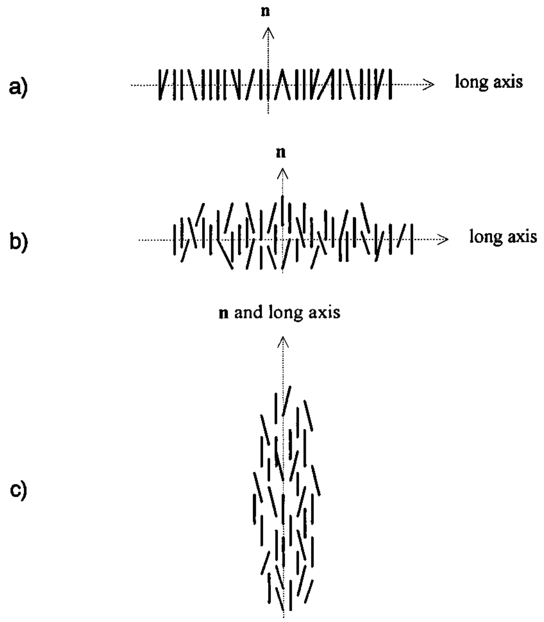

Figure 1. Schematic representation of three possible orientations of mesogens relative to the long axis of smectic and nematic domains. See text for details.

In this paper, we report a systematic investigation aimed at providing experimental evidence of the direct response of different mesophases to a mechanical force and reaching a better understanding on the orientation in SCLCPs. Two representative, polyacrylate-based SCLCPs were chosen and mechanically stretched in

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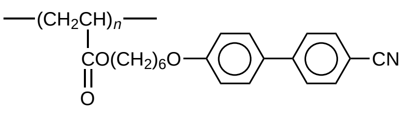
[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

their different mesophases. The macroscopic orientation of the mesogens, as well as that of the chain backbone, were determined through infrared dichroism. The results were analyzed in terms of our proposed mechanism.

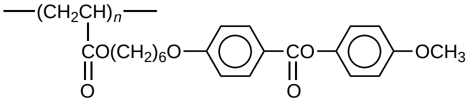
Experimental Section

SCLCP Samples. Two side-chain liquid crystalline polyacrylates were synthesized based on the procedure described in the literature.[6] The first polymer, referred to as BiPA-CN, has a biphenyl moiety as the mesogen which is ended with a C≡N group. Its molecular structure and the phase transition temperatures are as follows:



T_g 35 °C N_{re} 80 °C S_A 119 °C N 129 °C I

When cooled from the isotropic state (I), the polymer first enters into a nematic phase (N) at 129 °C, and then a smectic-A phase (S_A) at 119 °C, followed by an unusual reentrant nematic phase (N_{re}) at 80 °C before reaching the glass transition at 35 °C. As is shown, the second polymer, denoted as PA-OCH$_3$, carries a phenyl benzoate moiety as the mesogen and has an OCH$_3$ end group. It exhibits a nematic phase and a smectic-A phase, and the phase transition temperatures are as indicated.



T_g 25 °C S_A 94 °C N 119 °C I

It can be noted that both polymers have a quite long flexible spacer which contains six CH$_2$ units. Their mesophases were characterized by a Perkin-Elmer DSC-7 and a Leitz DMRP polarizing microscope. The measured transition temperatures are consistent with those reported in the literature, considering the differences in their molecular weights. The molecular weights were estimated by GPC using polystyrene standards. BiPA-CN has a number-average molecular weight, M_n, of 25 000 ($M_w/M_n = 1.5$), and PA-OCH$_3$ has an M_n of 12 700 ($M_w/M_n = 1.3$).

The reason of choosing these two SCLCPs is clear. Stretching them at temperatures covering all the mesophases makes it possible to investigate the alignment behavior of smectic phase, of nematic phase having a wide temperature range (45 °C for the re-entrant nematic phase of BiPA-CN and 25 °C in the case of PA-OCH$_3$), and also of nematic phase which appeared over a narrow temperature range (10 °C for the high-temperature nematic phase of BiPA-CN).

Mechanical Stretching. It has been some time since we realized the impossibility of preparing thin SCLCP films suitable to mechanical stretching and infrared dichroism measurements. In this study, we have employed one method developed in our laboratory which allows a SCLCP film to be mechanically stretched.[7] The method is schematically presented in Figure 2. The SCLCP film is obtained by solution-casting on the surface of a supporting film (ca. 80 μm thick) made from a 99% hydrolyzed poly(vinyl alcohol) (PVA). After drying, the PVA film can easily be stretched over a wide temperature range, and this leads to the stretching of the SCLCP film. In order to use this specific stretching approach, a significant interfacial interaction for adhesion between both films is necessary for the transfer of the mechanical field from PVA to SCLCP. As will be shown in this paper, we carried out experiments to make sure that the observed orientation behaviors, which constitute the basis for our analysis, did not arise from any kind of surface effects of the PVA film, but were truly due to the stretching effect. The details about this mechanical stretching procedure and the preparation of the film samples were described elsewhere.[7] In the present study, each stretching experiment consisted of annealing the film sample at 140 °C for 5 min (the SCLCP sample was in the isotropic state), bringing it to the stretching temperature for 15 min, then stretching it at a rate of about 50 mm/min, and finally quenching the deformed film at room temperature to preserve the macroscopic orientation. It is known that liquid crystallization from the isotropic state is a rapid phase transformation with a very small supercooling; therefore, under those conditions the samples before the stretching experiment should be very close to the equilibrium state. All films were uniaxially stretched to a draw ratio of about 3, i.e., ca. 200% deformation. Only the orientation in the plane of the films was measured in this study assuming, reasonably, a uniaxial symmetry of the orientation distribution along the stretching direction. And in all cases, the macroscopic orientation direction was considered with respect to the stretching direction.

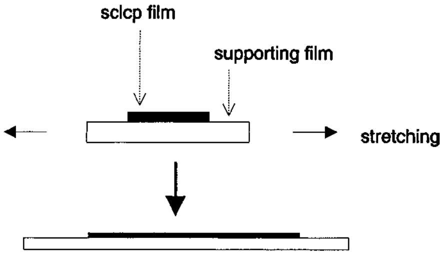


Figure 2. Schematic representation of the stretching method used. See text for details.

Orientation Measurements. Polarized infrared spectra were taken on the stretched films to determine the order parameter P_2 which is a measure of the orientation averaged over all the molecular units considered. Details on the use of infrared dichroism in our studies have already been reported.[7,8] In this study, the orientation of the flexible spacer could not be measured because of the overlap of the infrared bands of SCLCPs with those of PVA. The orientation of the mesogens and that of chain backbone were determined simultaneously. In the case of BiPA-CN, the C≡N band at 2230 cm^{-1} and the C=O band at 1735 cm^{-1} were used to measure the order parameter P_2 of the mesogens and that of chain backbone, respectively. For PA-OCH$_3$, the phenyl C−C stretching band at 1510 cm^{-1} allowed us to determine P_2 of the mesogens, but the use of the carbonyl band to measure P_2 of chain backbone was a little complicated by the presence of the other C=O in the phenyl ester group, both absorptions being superimposed at around 1735 cm^{-1}. P_2 of the chain backbone of PA-OCH$_3$ was calculated by separating the contributions from the two C=O units. If we define the infrared dichroic ratio of the C=O unit related to chain backbone as r' and that of the C=O unit in the mesogen as r'', we have

$$r' = A'_{\parallel}/A'_{\perp}$$

$$r'' = A''_{\parallel}/A''_{\perp}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances with the infrared beam polarized parallel and perpendicular, respectively, to the mechanical stretching direction. From the infrared spectra the measured dichroic ratio R of the 1735 cm^{-1} band is contributed by both C=O units:

$$R = (A'_{\parallel} + A''_{\parallel})/(A'_{\perp} + A''_{\perp}) \qquad (1)$$

r'' is related to P_2 of the mesogens through

$$P_{2,\mathrm{mesogen}} = (r_0 + 2)(r'' - 1)/(r_0 - 1)(r'' + 2)$$

where $r_0 = 2 \cot^2 \alpha$, α being the angle between the long axis of the mesogenic group and the transition moment of the C=O stretching vibration. As a first approximation, α can be taken as 60°, and we obtain

$$P_{2,\mathrm{mesogen}} = -8(r'' - 1)/(r'' + 2) \qquad (2)$$

As $P_{2,\mathrm{mesogen}}$ is known, being measured from the 1510 cm^{-1} band, r'' can be determined. Also, by assuming the same absorption for the two C=O units, we have

$$(A'_{\parallel} + 2A'_{\perp})/3 = (A''_{\parallel} + 2A''_{\perp})/3 \qquad (3)$$

Combining eqs 1−3, we obtain

$$r' = (2r'' - 4R - r''R)/(R - 2r'' - 2) \qquad (4)$$

For each stretched film of PA-OCH$_3$, knowing R and r'', r' is calculated from eq 4 and P_2 of the chain backbone can thus be determined.

All polarized infrared spectra were taken on a Bomen MB-102 FTIR spectrometer using a wire-grid polarizer placed between the sample and the DTGS detector. Unless otherwise stated, 50 interferograms and a 4-cm^{-1} resolution were used.

Results

Figure 3 shows examples of the polarized infrared spectra of stretched BiPA-CN films, with the electric field of the infrared beam parallel (∥) and perpendicular (⊥), respectively, to the stretching direction. In (a), the two spectra were recorded on a film stretched at 75 °C, i.e., in the re-entrant nematic phase. A strong parallel dichroism of the C≡N band as well as a perpendicular dichroism of the C=O band can be seen. This indicates a macroscopic orientation of the mesogens and that of chain backbone along the stretching direction. In (b), the two spectra indicate a reverse situation when the BiPA-CN film was stretched at 85 °C, in the smectic phase. The macroscopic orientation of the mesogens develops perpendicularly with respect to the stretching direction. The orientation of chain backbone is almost negligible, but a closer look reveals a very slight perpendicular alignment as well.

We performed the stretching experiment on BiPA-CN at temperatures between 55 and 140 °C, covering the different mesophases. The induced macroscopic orientation of the mesogens and that of chain backbone are shown in Figure 4, where P_2 is plotted as a function of the stretching temperature. Keeping in mind that positive P_2 values mean a parallel orientation (perfect orientation of all mesogens corresponds to $P_2 = 1$) and negative P_2 values mean a perpendicular orientation (perfect orientation is indicated by $P_2 = -0.5$), it is clear that the orientation behavior is strongly dependent on the mesophases. When BiPA-CN is stretched in the re-entrant nematic phase, a macroscopic orientation of the mesogens parallel to the stretching direction is induced. The P_2 values near 0.6 indicate an almost perfect alignment of the nematic directors along the stretching direction. The chain backbone is also oriented along the field direction, but the orientation is much lower than that of the mesogens. When BiPA-CN is stretched in the smectic phase, the mesogens change their orientation direction and are aligned perpendicularly with respect to the stretching direction. A sharp inversion of the orientation direction is revealed when the sample is stretched in the mesophase transition region. It is interesting to notice that, when the stretching is performed in the transition region, it is possible to induce zero macroscopic orientation for the mesogens, i.e., $P_2 = 0$. The other striking feature is that the chain backbone orientation also seems to change its direction in the transition region; a very slight perpendicular orientation can be seen with the samples stretched in the smectic phase. Now, when BiPA-CN is stretched in the high-temperature, narrow nematic phase, the perpendicular orientation persists for both mesogens and chain backbone. Finally, when the sample is stretched in the isotropic state, no orientation can be achieved.

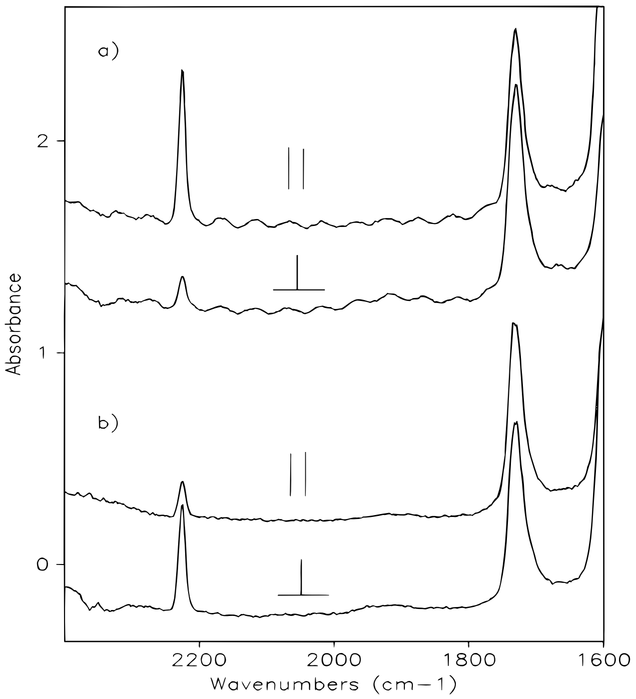


Figure 3. Polarized infrared spectra of two BiPA-CN films mechanically stretched at (a) 75 °C, in the re-entrant nematic phase, and (b) 85 °C, in the smectic phase, showing the inversion of the infrared dichroism. For each stretched film (draw ratio = 3), the two infrared spectra were obtained with the electric vector of the infrared beam parallel (∥) and perpendicular (⊥) to the stretching direction.

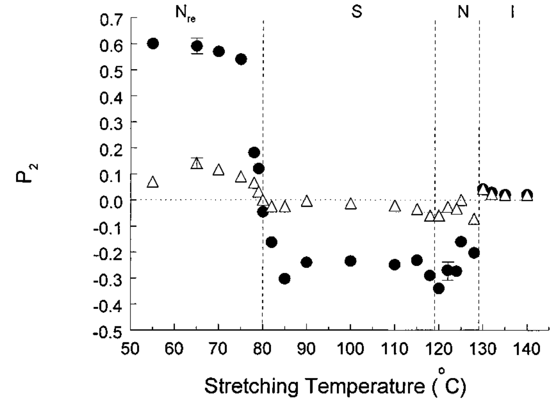


Figure 4. Order parameter P_2 of mesogens (●) and chain backbone (△) vs stretching temperature for BiPA-CN. Temperature ranges of different mesophases are indicated (draw ratio = 3).

The results obtained with PA-OCH$_3$ stretched in different phases are presented in Figure 5. In contrast with BiPA-CN, PA-OCH$_3$ has no re-entrant nematic phase at low temperatures, but a high-temperature nematic phase over a wide temperature range between the smectic phase and the isotropic state. As can be seen from Figure 5, the mesogens develop a perpendicular macroscopic orientation when PA-OCH$_3$ is stretched in the smectic phase and a parallel orientation when the stretching is done in the nematic phase. The inversion of the orientation direction is as sharp as that observed for BiPA-CN. Also like BiPA-CN, the chain

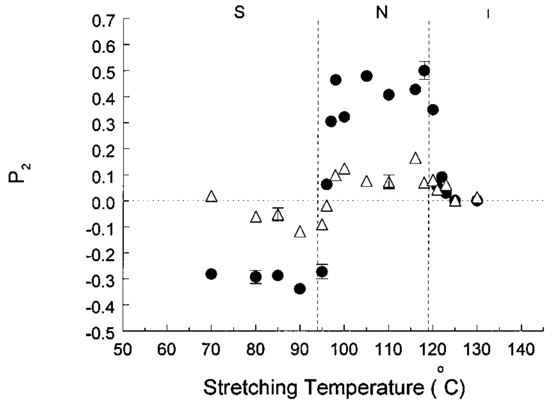


Figure 5. Order parameter P_2 of mesogens (●) and chain backbone (△) vs stretching temperature for PA-OCH$_3$. Temperature ranges of different mesophases are indicated (draw ratio = 3).

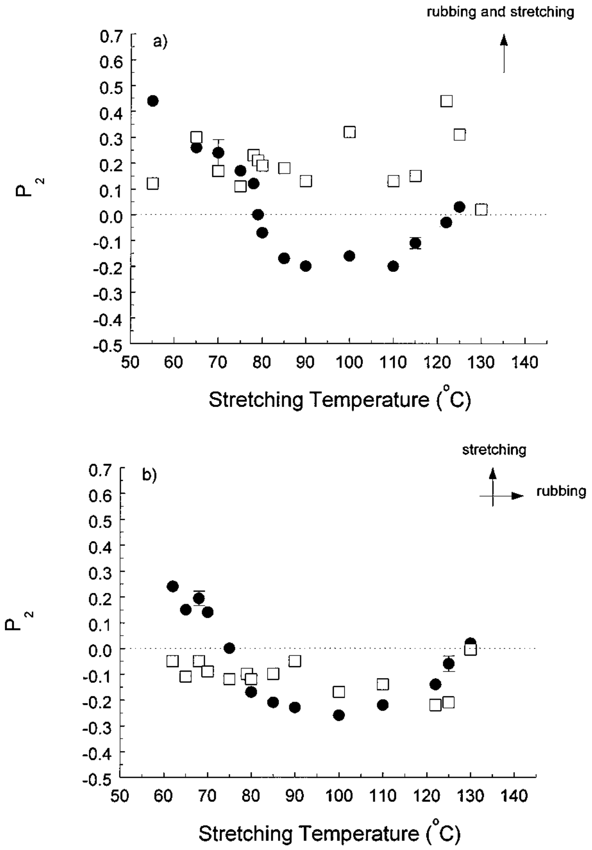


Figure 6. Order parameter P_2 of mesogens for BiPA-CN: (□) induced by surface effect of the rubbed PVA film before stretching, and (●) after mechanical stretching of the same films (draw ratio = 3). The stretching of the films was performed (a) along and (b) perpendicularly with respect to the surface rubbing direction.

backbone orientation is much lower, but seems to follow the mesogens, showing changes in the phase transition zone. And stretching in the isotropic state results in no orientation. In the case of SCLCPs subjected to a mechanical stretching, the monodomain structure generally is achieved after a draw ratio of about 2 or less,[5,7] which is indicated by an almost constant P_2 value at higher draw ratios. The draw ratio of 3 was chosen in the above stretching experiments to make sure that the alignment of the mesophases was essentially complete at each stretching temperature. This also partly explains the small scattering of the data of P_2 in Figures 4 and 5. It should be mentioned that the SCLCP films

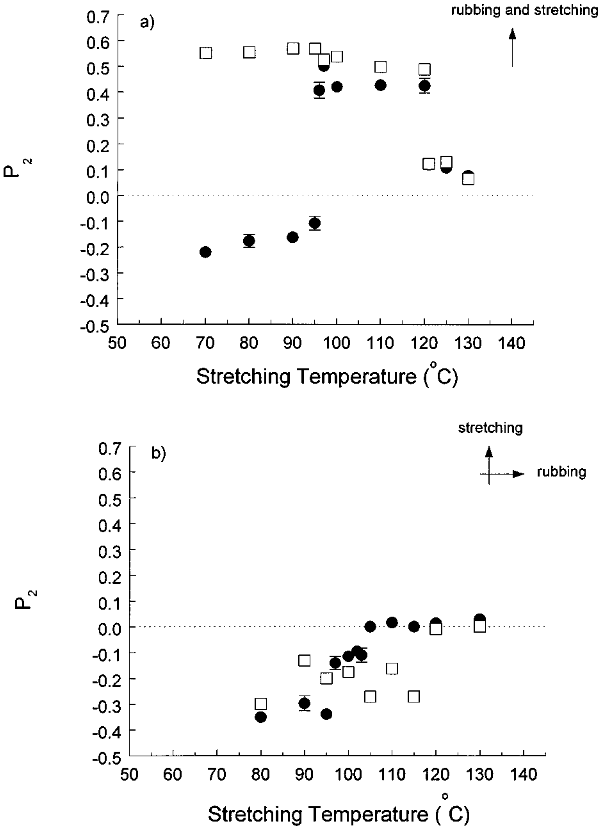


Figure 7. Order parameter P_2 of mesogens for PA-OCH$_3$: (□) induced by surface effect of the rubbed PVA film before stretching, and (●) after mechanical stretching of the same films (draw ratio = 3). The stretching of the films was performed (a) along and (b) perpendicularly with respect to the surface rubbing direction.

used were carefully controlled to have a similar thickness of ca. 20 μm.

In order to make sure that the observed orientation behavior in Figures 4 and 5 is, without ambiguity, the result of a mechanical stretching and reflects the mechanically-induced mesophase alignment, we performed a series of experiments which allowed us to rule out any possibility that the surface effects of the PVA supporting film had something to do with the observed results. The idea was to introduce, on purpose, a strong surface effect-induced macroscopic orientation of the mesogens before the mechanical stretching, and then to study the orientation behavior after the stretching of the same samples. For those experiments, PVA films with *rubbed* surface were used for the solution-casting of the SCLCP films. The prepared films were first annealed in different mesophases for 30 min, and the surface effect-induced orientation was measured at room temperature. Mechanical stretching of the films at different temperatures was then performed either along the rubbing direction or perpendicularly with respect to the rubbing direction. The macroscopic orientation of the mesogens after stretching was compared with their orientation induced by surface effect before stretching, and the results for BiPA-CN and PA-OCH$_3$ are given in Figures 6 and 7, respectively.

Obviously, the surface effect-induced orientation of the mesogens is always in the rubbing direction regardless of the mesophase, and the sign of P_2 is determined by the rubbing direction relative to the stretching direction, which are indicated in Figures 6 and 7. Therefore, with the stretching performed along the rubbing direction, the surface orientation before stretching has positive P_2 values, while for the stretching perpendicular to the rubbing direction the surface orientation is indicated by negative P_2 values. For the films stretched along the surface rubbing direction, it is clear that stretching BiPA-CN in the smectic and the high-temperature nematic phases (Figure 6a) and PA-OCH_3 in the smectic phase (Figure 7a) changes the parallel surface orientation to a perpendicular orientation, similar to that observed for the SCLCP films on PVA with nontreated surface after stretching (Figures 4 and 5). This is particularly evident in the case of PA-OCH_3. Despite the very strong parallel surface orientation, stretching in the smectic phase at temperatures between 70 and 95 °C results in an orientation perpendicular to the stretching direction. These results confirm that this perpendicular macroscopic orientation of the mesogens after stretching in the smectic phase or, for BiPA-CN, in the narrow, high-temperature nematic phase is truly due to an alignment of the mesophases under the action of a mechanical field. When PA-OCH_3 and BiPA-CN are stretched in the nematic phase and re-entrant nematic phase, respectively, the orientation remains to be parallel with P_2, apparently, close to that of the surface orientation before stretching. Now, similar observations can be made with the stretching performed perpendicularly with respect to the rubbing direction. Stretching BiPA-CN in the re-entrant nematic phase changes the perpendicular surface orientation to a parallel orientation (Figure 6b), while stretching PA-OCH_3 in the nematic phase brings a very strong perpendicular orientation to, apparently, no macroscopic orientation (Figure 7b). In both cases, the effect of a mechanically-induced alignment of the nematic phases toward a parallel orientation of the mesogens is clear. Here, a detailed analysis on the interplay between the surface orientation before stretching and the orientation achieved after stretching is outside the scope of this paper. Also, it should be mentioned that each data point of the surface orientation in Figures 6 and 7 represents a separate experiment with a new film, and the scattering of the data was mainly due to the differences in the SCLCP film thickness and in the surface rubbing procedure which was difficult to control and which could determine the efficiency of the surface alignment. However, examining the whole of the results, we can confirm, without any ambiguities, that the results given in Figures 4 and 5 reflect the alignment of different mesophases under the effect of a mechanical stretching.

Before discussing the mesophase alignment, it is worthwhile to report another experiment aimed at getting more insights into this specific stretching method which, we show, provides a convenient way to study the orientation phenomena in SCLCPs. Although we demonstrate that in our experiments no PVA surface effect is responsible for the observed macroscopic orientation averaged over all mesogens, an interesting question still remains as to what could happen in the interfacial region during the stretching. Strong interfacial interactions between SCLCPs and PVA certainly exist, since no stretching of SCLSPs can be induced if there is no interfacial interaction or adhesion between both films. With strong interfacial interactions, we could expect perturbation on the mesophases and different alignment behavior during the stretching. We prepared a series of very thin BiPA-CN films on PVA. The film thickness was less than 2 μm, i.e., reduced by at least 1 order as compared with the thick films used in the other stretching experiments described so far. All of the thin films were stretched in the smectic phase at 100 °C, and the induced orientation of the mesogens and that of chain backbone were measured (infrared spectra taken with 300−1000 scans). In Figure 8 is shown P_2 versus $(A_{\parallel} + 2A_{\perp})/3$ of the C≡N band which is a measure of the film thickness. It is seen that with a film ca. 2 μm thick the macroscopic orientation of the mesogens is still perpendicular to the stretching direction as for the thick films (Figure 4). But this perpendicular orientation lowers its magnitude as the film thickness further decreases, and eventually, the orientation direction is reversed when the film has an absorbance smaller than 0.027, which corresponds to an estimated thickness under 1 μm.[9] With the films having an absorbance ≤0.01 (thickness should be under 500 nm), the stretching results in a strong parallel orientation of the mesogens. This result suggests that in the region immediately neighboring the interface the stretching of PVA always leads to a parallel orientation of the mesogens whatever the mesophase supposed to be at the stretching temperature. Therefore, in this region the orientation is governed by the interfacial interactions effect and differs from the alignment under a mechanical field for the other regions more distant from the interface. Clearly, for relatively thick SCLCP films, with a thickness, say, above several micrometers, as this interfacial region is so small as compared with the remainder of the film, the observed macroscopic orientation reflects the alignment behavior under the mechanical stretching effect. In Figure 8, it can also be noted that for these thin films the orientation of chain backbone remains to be parallel to the stretching direction, both before and after the inversion of the orientation direction for the mesogens.

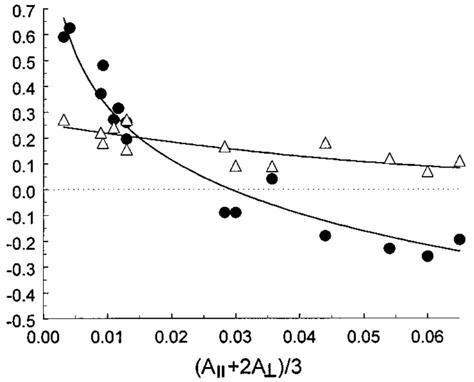


Figure 8. Order parameter P_2 of mesogens (●) and chain backbone (△) vs film thickness expressed by $(A_{\parallel} + 2A_{\perp})/3$ (absorbance of the C≡N band) for BiPA-CN mechanically stretched at 100 °C, in the smectic phase (draw ratio = 3).

Discussion

The results of our systematic orientation measurements after mechanically stretching two representative SCLCPs in their different mesophases suggest that the observed macroscopic orientation of the mesogens mainly reflects a direct alignment of the mesophases. It seems to be a common feature that stretching SCLCPs in their smectic phase gives rise to a macroscopic orientation of the mesogens perpendicular to the stretching direction (Figures 4−7). Both BiPA-CN and PA-OCH_3 exhibit a smectic-A phase; the former has a 25-Å-thick monolayer structure, and the latter has a partially bilayered structure of 34 Å thick.[10] As described in the Introduction, this corresponds to the situation (a) in Figure 1 since the smectic plane's normal is unlikely to coincide with the liquid crystalline domain's long axis. The observed perpendicular orientation of the mesogens could be the result of the alignment of the long axes of smectic planes along the stretching direction.

When BiPA-CN and PA-OCH$_3$ are stretched in their nematic phases, both parallel and perpendicular macroscopic orientation of the mesogens can be induced. In contrast with the smectic planes, the existence of anisotropic shapes for nematic domains is speculative at this point and needs to be confirmed by more studies. Nevertheless, the observed behaviors are consistent with the consequences of the suggested alignment of the long axes of nematic domains along the stretching direction. The high-temperature nematic phase of BiPA-CN, which exists over only a narrow temperature range of ca. 10 °C after the melting of the smectic phase and before the isotropization, seems to represent the situation (b) in Figure 1. In this nematic phase, it is reasonable to expect some kind of smectic fluctuations leading to a certain degree of layer ordering, whose existence in nematic phases was suggested by Brulet et al.[3] In other words, BiPA-CN in this region, being nematic, could have nematic domains "closer" to smectic layers with the nematic directors perpendicular to the domains' long axes. Consequently, the mechanical stretching still results in a perpendicular macroscopic orientation of the mesogens. On the other hand, the re-entrant nematic phase of BiPA-CN and the nematic phase of PA-OCH$_3$, both over a wide range of temperatures, should correspond to the situation (c) in Figure 1. Their nematic directors coincide with the domains' long axes. As the nematic domains align their long axes along the stretching direction, the observed macroscopic orientation of the mesogens is parallel.

On the other hand, the orientation of chain backbone is very low, often almost negligible, and seems to follow the inversion of the orientation direction manifested by the mesogens when BiPA-CN is stretched in the reentrant nematic to smectic (Figure 4) and PA-OCH$_3$ stretched in the nematic to smectic transition region (Figure 5). It is interesting to compare the mechanically-induced orientation observed in this study with the magnetic field-induced orientation for BiPA-CN or PA-OCH$_3$.[10] The magnetic field operates only on the liquid crystalline domains and aligns the mesogens along the field direction, regardless of the mesophases. When BiPA-CN is aligned in the re-entrant nematic phase and PA-OCH$_3$ in the nematic phase in a magnetic field, the small-angle neutron scattering measurements of Noirez et al.[10] revealed an anisotropic chain backbone conformation corresponding to a slight orientation in the same direction as the mesogens. When both polymers are aligned in their smectic phase, the observed anisotropic backbone conformation indicates a slight orientation perpendicular to the orientation direction of the mesogens. This was explained by the location of chain backbone between the smectic layers, and the confinement effect leads to a slight stretching of the chain backbone in the direction perpendicular to the smectic plane normal, i.e., perpendicular to the orientation direction of the mesogens. On the basis of the P_2 values obtained in the present study, the chain backbone seems to be slightly aligned always in the same direction as the mesogens (Figures 4 and 5). This is quite surprising for the stretching in the smectic phases, because if the confinement effect exerted by the smectic layers on the chain backbone is effective, a slight parallel orientation of chain backbone (positive P_2 values) should be observed as the orientation of mesogens is perpendicular to the stretching direction. Furthermore, judging from the small P_2 values, the direct mechanical stretching of the chain backbone must be very small.[11] One possible explanation is that the samples used in this study have relatively low molecular weights and, consequently, have no significant entanglements necessary for the stretching, which enhances the direct alignment of the mesophases. However, we mention that, under the same experimental conditions, a similar result, i.e., small P_2 of chain backbone which drops to zero when stretched in the isotropic state, was observed in a previous study[7] for an SCLCP sample having a much higher molecular weight ($M_w = 150\ 000$, $M_n = 86\ 900$).

Finally, we mention that the same stretching experiment at different temperatures was also performed on other SCLCPs in our laboratory. The results are consistent with those reported in this paper and support our analysis. For instance, the polyacrylate PA-CN, prepared by replacing the biphenyl moiety in BiPA-CN by a phenyl benzoate moiety, has only a nematic phase. The macroscopic orientation of the mesogens is always parallel to the stretching direction whatever the stretching temperature in the nematic phase.[7] Also, the polymer PMA-CN, which differs from PA-CN in having a polymethacrylate chain backbone, is mainly smectic, but displays a narrow nematic phase before the isotropization. A perpendicular orientation was observed with samples stretched in both mesophases.

Conclusions

The results of this study suggest that mechanically-induced macroscopic orientation of the mesogens in SCLCPs mainly reflects a direct alignment of the mesophases as a response to the mechanical field. The orientation direction of the mesogens is strongly dependent on the mesophase under the stretching effect, and a sharp inversion of the orientation direction can occur when the sample is stretched in the mesophase transition regions. Analyzing this change in the orientation direction could help us understand the mechanisms of the mesophase alignment. The whole of the results seem to support the view that liquid crystalline domains, being anisotropic in shape, orient as entities under the effect of a mechanical force and always align the domains' long axes along the stretching direction. On the basis of the observed behavior of BiPA-CN and PA-OCH$_3$, we can tentatively advance the following explanations. When SCLCPs are stretched in their smectic phase, the resultant orientation of the mesogens is perpendicular because the long axis of the smectic plane is not the plane's normal which is the orientation direction of the mesogens. When SCLCPs are stretched in the nematic phase, the orientation generally develops along the stretching direction because the "normal" nematic domains would have their long axes in the same direction as the nematic directors. But, for SCLCPs having a narrow nematic phase beyond the smectic phase, smectic fluctuations can lead to some layer ordering and, consequently, to nematic domains whose directors would be preferentially perpendicular to the domains' long axes; and the stretching results in a perpendicular orientation of the mesogens.

Acknowledgment. We thank Dr. Robert Prud'homme (Université Laval) for the use of GPC. Financial support of this reserach by the Natural Sciences and Engineering Research Council of Canada and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche of Québec is also gratefully acknowledged.

References and Notes

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(9) We obtained a calibration straight line by plotting the infrared absorbance of the C≡N band and some measured BiPA-CN film thickness between 2 and 6 μm. The thickness of thinner films was estimated through extrapolation of the calibration line, using the infrared absorbance.

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(11) We examined the stretching effect on the chain backbone of a non-liquid crystalline polymer, poly(ethyl methacrylate), cast on the surface of the PVA film. With a draw ratio of 3, stretching at 85 °C gave rise to $P_2 = 0.24$ and stretching at 123 °C led to $P_2 = 0.16$. The sample was purchased from Aldrich ($M_w = 340\ 000$, $M_n = 126\ 000$, $T_g = 68$ °C).

MA951672Q