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# Some reflections on the direction of the stress-induced macroscopic orientation of the mesogenic groups in side-chain liquid crystalline polymers: a new mechanism

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We propose a mechanism that can effectively determine the stress-induced orientation direction of the mesogenic groups in side-chain liquid crystalline polymers. The mechanism emphasizes the role of the ansiotropic shapes of the liquid crystalline domains and their direct coupling with the stress field. Examples are given to show that only the coupling effects between the polymer backbone and the mesogenic groups through the flexible spacer cannot explain all experimental observations. We suggest that, analogous to the smectic layers, the nematic domains could be anisotropic in shape. When a mechanical field is applied the nematic domains could directly be coupled to the stress field and, owing to the intermolecular cooperativity, respond to it by aligning their long axes preferentially along the field direction; consequently, the orientation of the mesogenic groups relative to the long axes of the domains prior to the mechanical alignment determines the macroscopic orientation direction of the mesogenic groups. We show that this mechanism accounts for a wide range of phenomena observed so far and can be corroborated by many complex, often apparently conflicting, experimental results. The mechanism also allows some predictions to be made.

**(Keywords: stress-induced orientation; mesogenic groups; liquid crystalline polymers)**

## INTRODUCTION

When side-chain liquid crystalline polymers (SCLCPs) or their elastomers are subjected to a mechanical stretching, a macroscopic and uniform orientation of the mesogenic groups can be induced. This leads to a transition from a polydomain to a monodomain structure. A feature of interest is that this macroscopic orientation can develop either along or perpendicular to the mechanical field direction. This phenomenon has not been understood yet, and many reported observations look apparently conflicting. Nevertheless, some factors affecting this orientation direction can now be identified owing to an increasing number of investigations. Firstly, for nematic SCLCPs, which generally have a short flexible spacer (two to six $CH_2$ units) linking the mesogenic groups and the chain backbone, the parity of the number of $CH_2$ units in the spacer often determines the orientation direction[1,2]. When the spacer has an even number of $CH_2$ units the orientation is preferentially parallel to the stretching direction, while when the spacer has an odd number of $CH_2$ units the orientation is perpendicular. Secondly, in some cases a perpendicular orientation can also be found for nematic SCLCPs which have six $CH_2$ units in the spacer[3,4]. This apparently is contradictory with the odd–even effect. Finally, smectic SCLCPs, which have longer flexible spacers (generally six or more $CH_2$ units), seem always to exhibit a perpendicular orientation on stretching[5-7].

Currently, the most prominent interpretation for the stress-induced orientation direction is mainly that of Mitchell and coworkers[2,8,9]. They have performed systematic investigations on the nature of the couplings between the polymer backbone and the mesogenic side groups on the basis of the theoretical models developed by Wang and Warner[10]. By denoting the nematic phase with the mesogenic units preferentially parallel to the attached chain backbone as $N_{III}$ (positive coupling) and the nematic phase with the mesogenic units arranged perpendicular to the chain backbone as $N_I$ (negative coupling), the approach of Mitchell and coworkers is to relate the nature of the coupling to the behaviour of the macroscopic orientation induced by the mechanical field. According to these authors, the coupling coefficient $\mu$ between the polymer backbone and the mesogenic groups is essentially composed of two contributions, $\mu = \mu_n + \mu_h$, where $\mu_n$ arises from the nematic-like interactions between the polymer backbone and the mesogenic groups, i.e. the mean nematic field effect, and $\mu_h$ characterizes the so-called hinge effect imposed between the two constituents through the flexible spacer. Basically, they presume, which is reasonable, that the mechanical force aligns the polymer backbone always along the field direction, and, as a consequence of the coupling, the mesogenic groups orient. The mean nematic field effect would always result in a parallel orientation for the mesogenic groups. The hinge effect, on the other hand, determines the orientation direction of the mesogenic groups depending on the nature of the nematic phase ($N_{III}$ or $N_I$) that is affected by the precise conformation or geometry of the spacer unit. Obviously, a positive coupling results in a parallel orientation, while a negative coupling leads to a perpendicular orientation. From the above argument, it is evident that the observed odd–even effect displayed by the flexible spacer suggests a dominant role of the hinge effect in the orientation direction[2]. Also, these authors suggest that the stress-induced orientation direction, in return, may be considered as being indicative of the nature of coupling in SCLCPs[2].

Though many experimental results seem to be consistent with the above interpretation, we feel some uneasiness with such a point of view that the mesogenic groups realign simply as the chain backbone orients and the nature of coupling decides the orientation direction of the mesogenic groups relative to the chain backbone and, thereby, to the mechanical field direction. All experimental observations cannot be explained in this way. For instance, the systematic perpendicular orientation observed for smectic SCLCPs and also in their nematic state at higher temperatures[5–7,11] can hardly be expected based on such an argument, since as the length of the flexible spacer increases the hinge effect should no longer prevail[2] and parallel orientation would be observed. In a recent study, Brûlet *et al.*[3] showed that a nematic, polymethacrylate-based SCLCP containing six $CH_2$ units in the spacer exhibited both a perpendicular and parallel orientation of the mesogenic groups when stretched at different temperatures between the glass transition temperature $T_g$ and the nematic to isotropic transition temperature $T_{ni}$. This result can hardly be accounted for by the hinge effect because it should not only be predominant with this long spacer but should also change the nature of coupling with temperature. Moreover, these authors have found that the relaxation of the chain backbone in the stretched samples did not affect the orientation of the mesogenic groups.

The other well-known result that looks incompatible with a predominant hinge effect is that upon stretching a monodomain structure is induced at a very small deformation of the sample (often < 50%), particularly for the elastomers; the orientation of the chain backbone at this point is much lower than the orientation of the mesogenic groups. For example, in the recent study of Mitchell *et al.*[2], the ratio of the backbone orientation to the orientation of the mesogenic groups has been estimated to range only from 0.005 to 0.012 for the polyacrylate-based elastomers investigated. The picture for these samples achieving a monodomain structure should be a perfect alignment of the nematic directors, with the polymer backbone having, however, only a very slight anisotropy relative to the random coil conformation. Such a situation has been confirmed by the recent investigation of Finkelmann *et al.*[12] using small angle neutron scattering. This means that the macroscopic orientation of the mesogenic groups is mainly completed at the early stage of the extension of the sample, during which most mesogenic groups realign in response to the mechanical field without orientation of the backbone segments anchored to them. This clearly contradicts a decisive role of the chain backbone alignment along the field direction in inducing the orientation of the mesogenic groups. It is interesting to note that this also means that whatever the macroscopic orientation direction of the mesogenic groups after the stretching, a large number of the side groups must necessarily lie preferentially both parallel and perpendicular to the chain segments anchored to them and in terms of the $N_{III}$ and $N_I$ nematic phases this should be a mixture of both. A last example of experimental results which raise questions is that when nematic SCLCPs are stretched at temperatures just below $T_{ni}$, say 2°C, the induced macroscopic orientation often is of a similar magnitude to when they are stretched at lower temperatures in the liquid crystalline state, but once they are stretched at $T > T_{ni}$ and under the same sample deformation, which presumably should lead to a similar backbone orientation, little or no orientation of the mesogenic groups can be observed[13].

Considering all of the above, it seems to us that the role of the coupling between the polymer backbone and the mesogenic groups through the hinge effect might be overrated, at least to some extent. We believe that other factors could determine, or contribute to, the stress-induced orientation direction of the mesogenic groups. An important aspect that certainly should not be neglected is the role of the intermolecular cooperativity associated with the liquid crystalline states. In this paper, we report our reflections on this subject by proposing a mechanism which is based on the response of the anisotropic microstructures in SCLCPs to a stress field. The idea will be confronted with the known experimental results. This mechanism should be considered as an alternative approach to interpret and understand the complex orientation behaviours in SCLCPs induced by a mechanical field. The purpose of this study is to incite further discussion and experimental investigations.

## THE PROPOSED MECHANISM

We have shown that many experimental observations, such as those described above, clearly demonstrate the importance of the intermolecular cooperativity associated with the liquid crystalline states in the achievement of a macroscopic orientation of the mesogenic groups. They also imply that the orientation behaviour of the mesogenic groups can be mostly independent of the polymer backbone. We suggest that the direct response of the nematic domains or the smectic layers to a stress field could be essential for determining the orientation direction of the mesogenic groups. When an SCLCP is subjected to a mechanical force, the build-up of the stress field acting on the mesogenic groups includes, of course, a stress transfer through the alignment of the chain backbone via the spacer, but the stress field can also be directly coupled to the side groups. The key point here is that the stress field should not only be considered as to couple to the individual anisotropic side groups, which would indeed align the long axes of the mesogenic groups along the field direction and always give rise to a parallel macroscopic orientation. The stress field could be more effectively coupled to the oriented microstructure, namely the nematic domains or the smectic layers. In the case of nematic SCLCPs, a nematic domain is generally defined as a region in which the mesogenic groups are preferentially oriented along a director, characterized by a local order parameter[14]. Before the application of a mechanical field (or other aligning fields), the overall orientation of the nematic directors is random throughout the sample, i.e. the sample has a

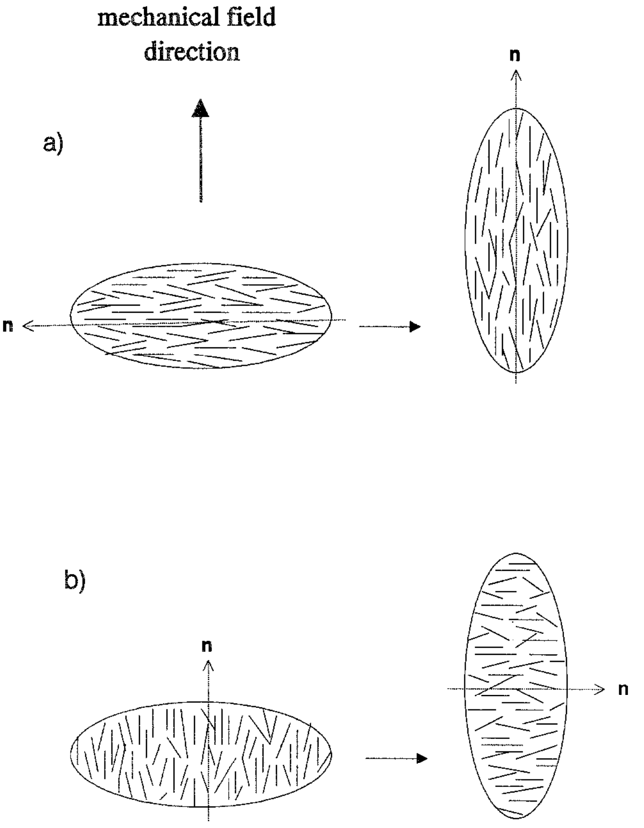


**Figure 1** Schematic representation of the alignment of the long axis of an anisotropic nematic domain along the mechanical field direction. The nematic director **n** can coincide with (a) the long axis or (b) the short axis of the nematic domain, resulting in an orientation of the mesogenic groups parallel or perpendicular, respectively, to the field direction

polydomain structure. The idea here is that the nematic domains, analogous to the smectic layers, could be strongly anisotropic in shape. When a domain is coupled with the stress field, all of the mesogenic groups within the domain could cooperatively respond as an entity, aligning the long axis of the domain along the field direction. The consequence of such a mechanism is that the relative orientation of the nematic directors with respect to the long axes of the domains prior to the stretching could be decisive for the direction of the stress-induced macroscopic orientation of the mesogenic groups. This is schematically illustrated in *Figure 1* by using, as an example, a nematic domain which is shaped like a rugby ball. When this anisotropic domain is under the effect of a mechanical field the long axis of the domain always aligns along the field direction. One possibility is that the nematic director coincides with, or is preferentially parallel to, the long axis of the domain (*Figure 1a*) and the resultant orientation for the mesogenic groups will be parallel to the mechanical field direction. In the other case (*Figure 1b*), where the nematic director is preferentially perpendicular to the long axis of the domain, after the alignment of the domain a perpendicular orientation of the mesogenic groups should be obtained. Essentially, this mechanism emphasizes the action of the stress field directly on the nematic domains and the reaction of the latter as entities. This is analogous to the magnetic alignment in the sense that the magnetic force is known to act on and align the nematic domains rather than individual mesogenic groups. However, for a mechanical alignment, instead of the anisotropy in the diamagnetic susceptibility, it is the anisotropy in the shape of the nematic domains, together with the intermolecular cooperativity, that is essential.

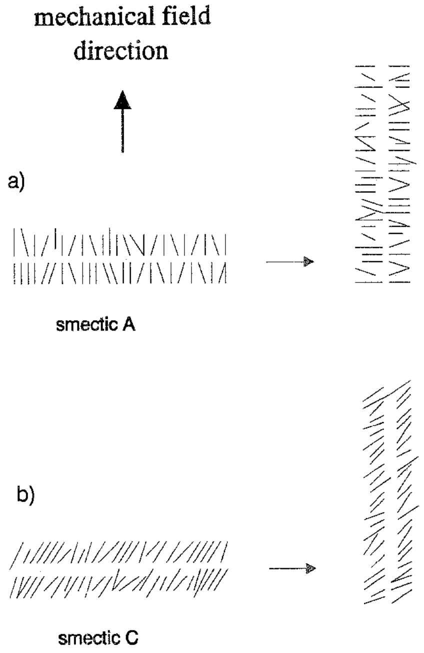


**Figure 2** Schematic representation of the alignment of the anisotropic smectic domains along the mechanical field direction. For both (a) smectic A and (b) smectic C, the stacking direction of the smectic layers is perpendicular to the field direction, which determines the orientation direction of the mesogenic groups

Extending this idea to smectic SCLCPs, it is easy to picture the situation as schematically shown in *Figure 2*. The smectic domains are highly anisotropic in shape, characterized by the planes of the smectic layers with the mesogenic groups being aligned preferentially parallel to the normal to the planes (smectic A) or along a direction making an angle with this normal (smectic C). In any case, it is more likely that the stacking direction of the layers does not coincide with the long axes of the domains. Consequently, the action of a mechanical field should align the smectic layers with the normal to the planes perpendicular to the mechanical field direction, as is illustrated in *Figure 2*. In other words, the planes of the smectic layers should be parallel to the field direction.

## EXPERIMENTAL CORROBORATION AND PREDICTIONS

It would be easy to confirm the proposed mechanism if we could observe the shapes of the nematic domains prior to their stretching and alignment under the mechanical field effect. Unfortunately, this is not an easy thing to do. For SCLCPs no such studies have been realized so far, and major technical difficulties are expected. In the case of main-chain LCPs, whose mesogenic groups are part of the chain backbone, some detailed investigations on the nematic domains have been reported[15-17]. Although elongated nematic domains were observed in some oriented samples[15], the results in those studies cannot be used to verify the orientation mechanism for a couple of reasons. Firstly, main-chain LCPs have a different molecular architecture from that of SCLCPs. This results in distinct orientation behaviours, and it would not be appropriate to use main-chain LCPs to analyse the mechanism proposed for SCLCPs. Secondly, the nematic domains investigated in those studies are generally not consistent with the exact definition of the nematic domains discussed in this paper. An apparent domain reflected, for example, by a light region seen in an optical microscope under crossed polarizers could be much larger than the domain as depicted in *Figure 1* because it could contain different domains with changing nematic directors that are not parallel or perpendicular to the polarizer. Therefore, it is clear that at this point it is impossible to test the proposed orientation mechanism through direct observation of the shapes and alignment of the liquid crystalline domains. The validity and generality of this mechanism can only be tested by confronting its expected consequences on the macroscopic orientation of the mesogenic groups with the known experimental results on SCLCPs.

The other thing that should also be pointed out is that this mechanism should be applied to SCLCPs and their lightly crosslinked elastomers. The crosslinks basically change the way that a stress field is coupled to the mesogenic groups, the nematic domains or smectic layers. The influences of the crosslinks have been clearly demonstrated[18]. At high crosslinking densities more complex situations should be expected. Now, applying the idea that the nematic domains or smectic layers can align through direct coupling with the stress field and that their anisotropic shapes can effectively determine the macroscopic orientation direction of the mesogenic groups, we discuss some typical experimental observations to establish the corroboration and, based on the analysis, make some predictions.

### *Odd–even effect*

For nematic SCLCPs containing a short spacer the odd–even effect seems to be general regardless of the type of the chain backbone[1,2]. Actually, this is the most prominent example which apparently shows a predominant hinge effect on the macroscopic orientation of the mesogenic groups. As has been discussed earlier, to account for this effect a change in the precise geometry of the spacer unit due to the change in the parity of the number of $CH_2$ units has been proposed[2], which leads to mesogenic groups lying more parallel or perpendicular to the chain backbone. Now, in terms of the proposed mechanism with the alignment of the anisotropic nematic domains under the effect of a stress field, the odd–even effect can be explained by a change in the nematic directors relative to the long axes of the nematic domains formed. Apparently, it seems to indicate that with an even number of $CH_2$ units in the spacer the nematic domains formed have their directors more parallel to the long axes of the domains, while when the spacer contains an odd number of $CH_2$ units the nematic directors are more likely to coincide with the short axes of the nematic domains. Of course, this is speculation as long as there is no direct experimental evidence. What is interesting to mention, however, is that a change in the nematic directors relative to the long axes of the domains could occur if we assume an anisotropic shape for the domains and that the position of the mesogenic side groups with respect to the chain backbone changes from parallel ($N_{III}$) to perpendicular ($N_I$) as has been suggested for explaining the hinge effect[2]. Such a change is schematically depicted in *Figure 3*, where the nematic director changes from being parallel to the long axis of the domain to the position coinciding with the short axis of the domain while the mesogenic side groups change their orientation relative to the chain backbone. It should be emphasized that *Figure 3* is set to explain the point and we have no experimental evidence to suggest, as can be noticed in this figure, that the nematic director coincides with the long axis of the domain when the mesogenic groups lie parallel to the chain backbone.

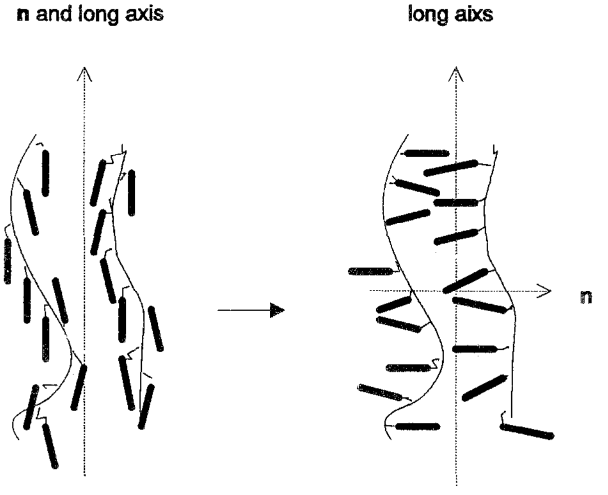


**Figure 3** Schematic representation of the change in the nematic director with respect to the long axis of the nematic domain, resulting from a change in the orientation of the mesogenic side groups relative to the chain backbone

### *Smectic SCLCPs*

The smectic domains are highly anisotropic in shape, and their alignment behaviours in response to a mechanical field could be predicted as schematically shown in *Figure 2*; that is, the stacking direction of the layers, or the normal to the plane, is in the direction of the short axis of the domain and should be aligned perpendicular to the stress field direction. In other words, for SCLCPs exhibiting a smectic A phase, whatever the length of the flexible spacer and the parity of the number of $CH_2$ units it contains, when stretched in the smectic state the resultant macroscopic orientation of the mesogenic groups would always be perpendicular to the stress field direction. Moreover, for those samples displaying a nematic phase at higher temperatures before the isotropization process, it could be expected that when stretched at temperatures relatively close to the smectic to nematic transition, a systematic perpendicular orientation would persist because, although the layer structures are absent, it is likely that the formed nematic domains stay strongly anisotropic in shape with the mesogenic groups lying in the direction of the short axes of the domains. This is schematically illustrated in *Figure 4*. The experimental results on smectic SCLCPs reported so far[4–7] and some observations in our own laboratory[11] are in good agreement with this prediction

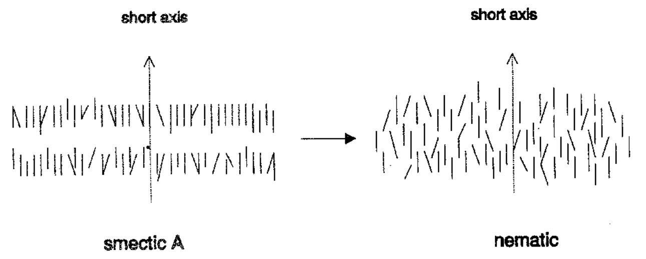
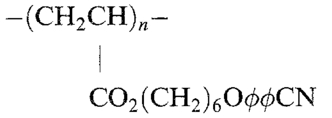


**Figure 4** Schematic representation of a phase transition from smectic A to nematic, leading to a nematic domain anisotropic in shape and whose short axis coincides with the nematic director. In this case the stress-induced orientation of the mesogenic groups should be perpendicular to the mechanical field direction

based on the mechanism, revealing a perpendicular macroscopic orientation. For the smectic samples having a large nematic phase, when stretched at temperatures close to $T_{ni}$ the situation could be changed with nematic directors more parallel to the long axes of the domains and a parallel macroscopic orientation could be observed. For SCLCPs stretched in their smectic C phase, it could be predicted that a lower perpendicular orientation of the mesogenic groups would generally be achieved because of the tilt angle (*Figure 2b*). Actually, depending on the tilt angle it would even be possible to observe no macroscopic orientation through stretching of the samples.

The use of a polyacrylate-based SCLCP can be of particular interest to test the mechanism. It has the following chemical structure



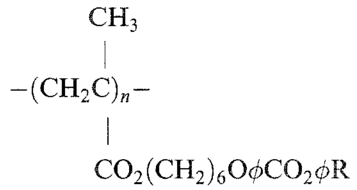
$$\begin{array}{c}-(CH_2CH)_n-\\ |\\ CO_2(CH_2)_6O\phi\phi CN\end{array}$$

where $\phi$ denotes the phenyl group. This polymer displays a rich polymorphism. When it is cooled from the isotropic state it exhibits an isotropic to nematic transition at about 122°C, then a nematic to smectic A transition at 112°C, and, more interestingly, a re-entrant nematic phase at lower temperatures between its $T_g$ (35°C) and 83°C. Noirez *et al.*[19] have studied the polymer backbone conformations in all these phases by small angle neutron scattering, and with samples whose mesogenic groups were aligned in a magnetic field. They found an oblate backbone conformation in the smectic A phase and, although much less clear, in the high temperature nematic phase as well. However, a prolate conformation was found in the re-entrant nematic phase. Without discussing the coupling between the backbone and the mesogenic groups involved in these magnetic experiments, what we are interested in here is that the nematic domains in these two nematic phases are revealed to be different. In the high temperature nematic phase the nematic domains must be closer to the smectic domains as has been discussed above with *Figure 4*, but in the re-entrant nematic phase the nematic domains would contain many fewer elements of a layer ordering. Therefore, based on the proposed mechanism it can be predicted that when this polymer is stretched in the smectic A and the high temperature nematic phases the macroscopic orientation of the mesogenic groups would be perpendicular to the stretching direction, while when it is stretched in the re-entrant nematic phase at lower temperatures a parallel orientation would be observed. Some results reported by Shibaev[7] on this polymer subjected to a shearing force support the prediction. However, it is worthwhile to perform systematic investigations on samples stretched in these three phases.

### *SCLCPs containing six $CH_2$ units in the spacer*

These polymers represent an interesting group of samples. Their flexible spacer is long enough to reduce very significantly the coupling between the polymer backbone and the mesogenic groups. This often allows the formation of a smectic A phase at lower temperatures. The existence of a smectic A phase is very sensitive to the type of the mesogenic moieties and the terminal end-groups attached to them. Clearly, when there are six $CH_2$ units in the spacer the polymer is often situated in the frontier zone between the nematic and smectic A regimes and often displays both mesophases. Keeping the proposed mechanism in mind, this situation explains why a perpendicular macroscopic orientation of the mesogenic groups is often achieved on stretching even for the nematic polymers, in spite of the even number of $CH_2$ units in the spacer.

Among the SCLCPs containing six $CH_2$ units in the spacer, the polymethacrylate-based samples bearing a phenyl benzoate moiety in the side group are the most studied. They have the following chemical structure



$$\begin{array}{c}CH_3\\ |\\ -(CH_2C)_n-\\ |\\ CO_2(CH_2)_6O\phi CO_2\phi R\end{array}$$

where R is the end-group. An interesting example of the experimental results which corroborate the proposed mechanism can be found in the recent study of Brûlet *et al.*[3], who studied the polymer with $R = CH_3$. The polymer is basically nematic between its $T_g$ (45°C) and $T_{ni}$ (82°C). The authors found that when it was stretched at 77°C the mesogenic groups were oriented along the stretching direction, while when it was stretched at 55°C the orientation was revealed to be perpendicular to the stretching direction, and they attributed the perpendicular orientation to be due to strong smectic A fluctuations that occurred at 55°C. These results can be explained by the alignment of the long axes of the anisotropic nematic domains, as is schematically depicted in *Figure 5*. At higher temperatures like 77°C there would be 'normal' nematic domains with the nematic directors coinciding with, or lying preferentially parallel to, the long axes of the domains, and the stress-induced orientation of the mesogenic groups should be parallel to the stretching direction. At lower temperatures like 55°C the strong smectic A fluctuations result in anisotropic domains with layer ordering, in which the mesogenic groups are oriented more parallel to the short axes. As the domains respond to the stress field always by aligning their long axes along the field direction, the resultant orientation of the mesogenic groups becomes perpendicular. For the SCLCPs having the above structure but differing in the end-group R, it can be expected that this kind of behaviour could be observed for other polymers that are nematic but close to the formation of a smectic A phase at lower temperatures. A

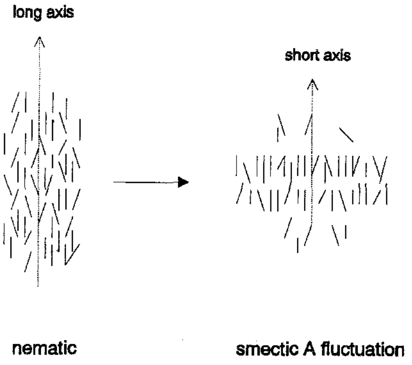


**Figure 5** Schematic representation of the smectic A fluctuations in a nematic domain when the sample temperature is lowered, which leads to a change in the orientation of the mesogenic groups relative to the long axis of the domain. When the sample is stretched in the two regimes, parallel and perpendicular macroscopic orientations of the mesogenic groups should be observed with respect to the mechanical field direction

probable example is the polymer with $R = OCH_3$. Also, still for this group of samples, it has been shown[20] that for the polymers with $R = CN$, $OC_4H_9$ or $\phi$ (phenyl ring), a smectic A phase starting from 10–20°C below the $T_{ni}$ could be detected by X-ray diffraction experiments but could not be detected by polarized optical microscopy which only showed a typical nematic texture. It is interesting to see that these polymers are still 'balanced' between the nematic and smectic A regimes, but they are closer to smectic A than the one with $R = CH_3$ which only exhibits smectic A fluctuations. Therefore, for these three polymers, whatever the stretching temperature below $T_{ni}$ is, it would be difficult to observe a parallel orientation of the mesogenic groups relative to the stretching direction, and a perpendicular orientation would be expected instead. We have examined one of these polymers, the one with $R = CN$, and this is exactly what is observed[11].

More interestingly, we can see that the proposed mechanism reconciles the conditions leading to a perpendicular orientation, which are apparently different and even conflicting. The anisotropic shape of the smectic layers is mostly evident, and the mechanism expects a perpendicular orientation on stretching (*Figure 2*). Now, starting from the smectic layers, the above analysis clearly reveals that for nematic SCLCPs a perpendicular orientation is observed when the stress field operates under such conditions that the polymers tend to approach to the smectic regime and form some layer ordering. Under these conditions, the polymers, being still nematic, have nematic domains which are 'closer' to the smectic layers and, as a consequence anisotropic in shape, with the mesogenic groups lying preferentially parallel to the short axes. This is the case for many nematic polymers having six $CH_2$ units in the spacer, for the polymers stretched just beyond the smectic to nematic transition, and probably also for the nematic polymers that have a short spacer containing an odd number of $CH_2$ units. In this last case, the possibility that the mesogenic groups are more perpendicular to the chain backbone could favour a higher extent of layer ordering.

### *Zero macroscopic orientation*

An interesting phenomenon has been revealed by the recent studies of Brûlet *et al.*[3] and Mitchell *et al.*[8]. Under some circumstances no macroscopic orientation of the mesogenic groups can be induced through mechanical stretching, even under a high extension of the sample. In the study of Brûlet *et al.*, this occurred when the polymer, i.e. the one discussed in the preceding section, was stretched at 67°C. This temperature has been described as a crossover between the two regimes of the nematic (e.g. 77°C) and the fluctuating smectic A phase (e.g. 55°C) that led to a parallel and a perpendicular orientation, respectively. On the other hand, Mitchell *et al.*[8] have prepared a series of random copolymers from two acrylate monomers containing, respectively, two and three $CH_2$ units in the spacer. Aimed at investigating the opposing influences originating from the odd–even effect, the situation of zero macroscopic orientation was observed for a copolymer containing 75 mol% of the monomeric units with three $CH_2$ units in the spacer. On the basis of the definitions of $N_{III}$ and $N_I$, these authors have introduced the concept of the $N_0$ nematic phase with a zero coupling between the polymer backbone and the mesogenic groups to explain this phenomenon. Basically, it is suggested that for SCLCPs exhibiting the $N_0$ nematic phase when the polymer backbone is aligned along the stress field direction, the mesogenic side groups show no macroscopic orientation because they have no preference to realign parallel or perpendicular to the chain backbone. It would be interesting to investigate the magnetic alignment of those samples showing no stress-induced orientation of the mesogenic groups in order to confirm the zero coupling situation. In contrast with the mechanical field, the magnetic force only acts on the mesogenic groups and any orientation of the chain backbone should be due to the coupling effect between the two constituents. Now, in terms of our proposed mechanism based on the response of the anisotropic nematic or smectic domains, a natural prediction is that a zero macroscopic orientation of the mesogenic groups upon stretching would be observed for SCLCPs in two cases: (1) the liquid crystalline domains, mostly nematic, are not clearly anisotropic in shape, i.e. no clear long axis can be defined and the effective axial ratio is close to unity; and (2) the nematic directors relative to the long axes of the domains are random throughout the sample. Under these conditions the mechanical field could align the nematic domains but results in no macroscopic orientation of the mesogenic groups. Such a situation could exist for a sample undergoing a transition between two regimes in which the orientation of the mesogenic groups with respect to the long axes of the domains is preferentially parallel or perpendicular, respectively (*Figure 5*). This would explain the observations of Brûlet *et al.*[3]. This particular situation could also be encountered for a random copolymer composed of two monomeric units which favour the formation of nematic domains whose long axes are preferentially parallel and perpendicular, respectively, to the orientation of the mesogenic groups. This would explain the results of Mitchell *et al.*[8].

### *Fibre drawing from the isotropic state*

It is worthwhile to give more details for one particular case. All of the above analysis obviously is based on applying a mechanical field to SCLCPs in their liquid crystalline states. However, fibre drawing from the isotropic state is a method quite often used to stretch SCLCPs mechanically[5,21]. Under these conditions the nematic domains or smectic layers are obviously absent during the stretching, and the orientation behaviour of the mesogenic side groups should be governed by the alignment of the chain backbone and the preferential orientation of the side groups relative to them. However, the data on orientation obtained in this way should be interpreted with caution. In a recent study[22] we have found that for some SCLCPs when they were stretched in the isotropic state, little or no macroscopic orientation of the mesogenic groups was induced, but eventually after quenching under strain a macroscopic and uniform orientation was achieved. Studying the underlying mechanisms, we found that the observed macroscopic orientation occurred rapidly during the cooling process while the sample under strain, i.e. under the effect of a mechanical field, entered into the nematic state. Therefore, when SCLCPs are stretched through fibre drawing from the isotropic state, it should be remembered that during the subsequent quenching process, once the polymer enters into the liquid crystalline states there could be a rapid response of the nematic domains or smectic layers to the stress field still acting on the deformed sample at this point, and this can contribute to most of the orientation observed afterwards. Clearly, if this orientation mechanism predominates, the rate of the quenching process could affect the achieved orientation of the mesogenic groups.

## CONCLUSION

For SCLCPs and their lightly crosslinked elastomers, we have proposed a mechanism that can effectively determine the direction of the stress-induced macroscopic orientation of the mesogenic groups with respect to the mechanical field direction. The idea is that the response of the intrinsically oriented microstructure, i.e. the nematic domains or smectic layers, to the stress field can be essential to the observed orientation behaviour. The liquid crystalline domains can be strongly anisotropic in shape and, owing to the intermolecular cooperativity, they can respond to the stress field as entities by aligning their long axes along the field direction. Consequently, the relative orientation of the mesogenic groups within the domains prior to the stretching determines the macroscopic orientation direction. Our analyses show that for the nematic SCLCPs whose nematic directors lie preferentially parallel to the long axes of the domains, the macroscopic orientation should be parallel to the mechanical field direction, while for the nematic SCLCPs whose nematic directors lie preferentially perpendicular to the long axes of the domains, the macroscopic orientation should be perpendicular. In the case of smectic SCLCPs, as the stacking direction of the layers is likely to coincide with the short axes of the domains, which should be perpendicularly aligned in response to the stress field, it can be expected that all smectic A polymers would exhibit a stress-induced perpendicular orientation of the mesogenic groups, and that such a perpendicular orientation would be less important for smectic C polymers because of the tilt angle. We have shown that this mechanism accounts for a wide range of orientation phenomena observed so far and is corroborated by many complex, and often apparently conflicting, experimental results.

Our proposed mechanism emphasizes the role of the aniostropic shapes of the liquid crystalline domains and their direct coupling with the stress field in the macroscopic orientation of the mesogenic groups. This is fundamentally different from the interpretations that make the orientation of the polymer backbone and the nature of its coupling with the mesogenic groups the most decisive factors in the macroscopic orientation direction of the mesogenic groups. Without ruling out the importance of the coupling between the polymer backbone and the mesogenic groups, the interest of this study was to introduce the importance of the intermolecular cooperativity associated with the liquid crystalline states and to advance a new approach of analysis in the search for understanding of the stress-induced orientation behaviour in SCLCPs. For example, on the basis of the reflections reported in this paper, it would be important to study the evolution of the shapes of the nematic domains and the ways in which they can be coupled with the different kinds of mechanical fields (extensions, shearing, compression, etc.). Although at this point the anisotropic shapes of the nematic domains and the alignment of the long axes of the domains along the mechanical field direction cannot easily be confirmed by direct experimental observations, our whole analysis in conjunction with the anisotropic smectic layers and their transitions to the nematic domains clearly supports the validity of these key points. The effects of the anisotropic shapes of the liquid crystalline domains on the macroscopic orientation of the mesogenic groups can only be elucidated through careful and systematic investigations.

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