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Side-chain liquid crystalline ionomers: 3. Stress-induced orientation in blends with poly(vinyl chloride) as matrix

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The mechanically induced macroscopic orientation in two series of side-chain liquid crystalline ionomers was investigated in order to reveal the effects of the ionic aggregates. The ionomer samples, which contained a small amount of COO^-Na^+ groups (< 10 mol%), were prepared through partial hydrolysis, using sodium hydroxide, of two liquid crystalline polyacrylates differing in the mesogenic units. The application of a mechanical field was rendered possible by blending these samples with an immiscible poly(vinyl chloride) matrix and stretching the blend films obtained by solution-casting. Comparisons were made between the ionomers having different ion contents and the initial polymers containing no ionic groups, and very distinct orientation behaviours were observed for the two series of ionomers. In the case of the ionomers prepared from a polyacrylate having a biphenyl moiety in the side group, the stress-induced orientation of the mesogenic units was found to be almost unchanged with respect to the polymer, judging from the orientation development upon extension, the level of the achievable orientation, and the common feature that a macroscopic orientation could only be obtained by stretching the sample in the nematic state. In contrast, for the ionomers based on a polyacrylate carrying a phenyl benzoate moiety, the ionic aggregates showed strong effects on the macroscopic orientation; the achievable orientation was found to be systematically lowered as the ion content in the ionomer was higher. Moreover, it was found, surprisingly, that the macroscopic orientation could be induced even when the samples were stretched in the isotropic state, with the same level as the samples stretched in the nematic state. Studying the underlying mechanisms, we found that when stretching the samples at $T > T_{ni}$ (the nematic to isotropic transition temperature), the observed macroscopic orientation was totaly achieved during the cooling of the samples under strain, while when stretching at $T < T_{ni}$, a partial macroscopic orientation was first induced by the stretching and the orientation was further improved during the cooling. Different factors which could play a role in this peculiar orientation process are discussed.

(Keywords: side-chain ionomers; stress-induced orientation; poly(vinyl chloride))

INTRODUCTION

One important aspect of the research on side-chain liquid crystalline polymers (LCPs) is the control and manipulation of the macroscopic orientation of the mesogenic units under effects of external fields such as magnetic, electric and mechanical forces. Among the many factors which can affect the orientation process, it is of interest to know the correlation between the macroscopic orientation and the intrinsically oriented microstructure which characterizes the mesophases in LCPs. To conduct this kind of investigation it is necessary to use samples with changing mesophase behaviour, but keep unchanged other parameters, such as the degree of polymerization and the length of the flexible spacer linking the mesogenic units to the chain backbone. Recently we have prepared LC ionomers through partial alkaline hydrolysis of LC polyacrylates[1]; these samples meet the requirements, since the random incorporation of a small amount, generally < 10 mol%, of ionic groups results in a perturbation of the microstructures and, consequently, a systematic depression of the nematic to isotropic transition temperature T_{ni} without, interestingly, much affecting the associated transition enthalpy and the glass transition temperature T_g. This disturbing effect is mainly due to the formation of ionic aggregates in the ionomers[2], which reduce the polymer chain mobility and increase the internal elastic constraints for the mesogenic units.

In a previous study[3], the macroscopic orientation of some ionomers in a strong magnetic field, as well as the initial polyacrylate containing no ionic groups, was investigated. The ionic aggregates were found to exert strong effects on the achievable magnetic alignment. As part of the research programme, this paper reports a study focused on the macroscopic orientation of the ionomers subjected to a mechanical field. Studying mechanically induced orientation was usually performed on side-chain LC elastomers[4,5] which, through formation of a network structure, possess the good deformability required for mechanical stretching. For the case of non-crosslinked LCPs, an alternative, which

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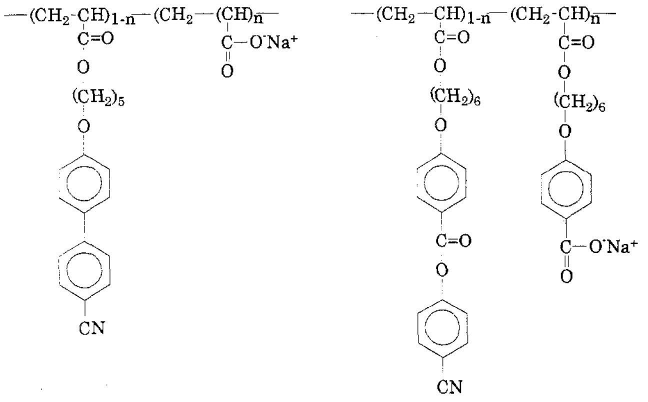
Table 1 Chemical structures and phase transition temperatures of the samples


Series A Series B

Sample	n (mol%)	T_g (°C)	T_{ni} (°C)
A1	0	38	117
A2	7	37	107
A3	9	37	88
B1	0	30	122
B2	2.5	28	106
B3	5.3	25	90
B4	7.3	24	72

enables one to investigate the stress-induced orientation behaviour, is to stretch a supporting medium made from a conventional polymer, i.e. a film onto whose surface a LCP film is cast or a polymer matrix in which a LCP is dispersed[6,7]. These methods allow a mechanical field to be applied on the LCP sample and are efficient enough to promote a macroscopic orientation with a level similar to that for the LC elastomers. This is why, for the present study aimed at revealing the effects of ionic aggregates on the stress-induced orientation, we have chosen the experimental approach of blending the LCP samples (10 wt%) in a poly(vinyl chloride) (PVC) matrix and stretching the blend films. In this way, we have been able not only to observe the orientation behaviour of the ionomers but also to reveal the underlying mechanisms involved in the orientation process under a stress field.

EXPERIMENTAL

Two series of ionomers were used, prepared through partial hydrolysis, using sodium hydroxide, of a polyacrylate bearing a biphenyl moiety in the side group and of a polyacrylate carrying a phenyl benzoate moiety: the samples are referred to as series A and series B, respectively. Their chemical structures, as well as the phase-transition temperatures determined by differential scanning calorimetry (d.s.c.) (Perkin-Elmer DSC-7, 10°C min^{-1} heating rate), are given in *Table 1*. The mole percentages of the ionic groups (COO^-Na^+) are expected values based on the amount of NaOH used in the reactions. Details about the synthesis and characterization of the ionomers are given elsewhere[1]. For the initial polymers containing no ionic groups, A1 has $\bar{M}_n \approx 79\,000\,g\,mol^{-1}$ ($\bar{M}_w/\bar{M}_n = 1.78$), and B1 has $\bar{M}_n \approx 47\,000\,g\,mol^{-1}$ ($\bar{M}_w/\bar{M}_n = 1.54$), as estimated by gel permeation chromatography (g.p.c.) using polystyrene as standards.

All the samples were blended with PVC (Aldrich, $\bar{M}_n = 37\,500\,g\,mol^{-1}$) in a weight-based ratio of 10/90. Thin blend films, about 40 μm thick, were obtained from solution-casting. For the series A samples, tetrahydrofuran was used as the solvent while dimethylsulfoxide was used for series B (the solutions were heated for dissolving both polymers and cast onto the surface of preheated glass plates). After evaporation of most solvent, the films were further dried under vacuum at 60°C for several days. Prior to the mechanical stretching experiments, the film samples were annealed, in vacuum, at 130°C for 10 min.

Mechanical stretching of the films (10 mm in length and 8 mm in width) was performed on a hand-driven apparatus, which was placed in a temperature-controlled oven (±1°C). The strain rate was about 50 mm min^{-1}; and, unless otherwise stated, the films were cooled under strain at room temperature immediately following the stretching, in order to preserve the macroscopic orientation. The extension of the films was measured by determining the draw ratio λ, defined as $\lambda = l/l_0$, l_0 and l being the film lengths before and after stretching, respectively.

The order parameter P_2 was used to characterize the macroscopic orientation and determined through the well known infra-red dichroism method. P_2 is a measure of the average orientation over all the molecular units considered (mesogenic groups or chain segments). Although we were mainly interested in the orientation of the mesogenic groups, for some experiments the P_2 of the matrix PVC was also measured for comparison. Details on the use of infra-red dichroism in our studies have already been reported[6,7]. Here, we mention that for the calculation of the P_2 of the mesogenic groups, all infra-red absorbances were lower than about 0.2, ensuring the validity of Beer's law. Also, the uniaxial stretching of the samples, i.e. the fibre symmetry, has been checked by observing the absorbance which, within the error of the measurements, was proportional to $1/\lambda^{1/2}$. The polarized infra-red spectra were recorded on a Bomen-MB102 FTIR spectrometer.

RESULTS AND DISCUSSION

As mentioned in the Introduction, in the present work PVC was used essentially as a matrix for realizing the stretching experiments. The choice of PVC was based on the requirement of stretching most LCP samples in their nematic state. Although the resulting blends were expected to be phase-separated, it was interesting to characterize the blend samples since significant interfacial interactions could exist. For these blends it is reasonable to assume that upon stretching, the mechanical force mainly operates on the PVC matrix (90% by weight) and the interfacial interactions could play a role in the transfer or build-up of a stress field effectively acting on the LCP samples, thereby affecting the macroscopic orientation of the mesogenic groups. D.s.c. measurements were performed on the blend samples, confirming the phase-separated character. Two representative examples of the d.s.c. heating curves, recorded for the blends with A2 and B2, respectively, are given in *Figure 1*. In both cases, two T_gs can clearly be seen; one, arising from the LCP phase, appeared at around 30°C while the other, belonging to the PVC matrix, was at about 70°C. In the case of the

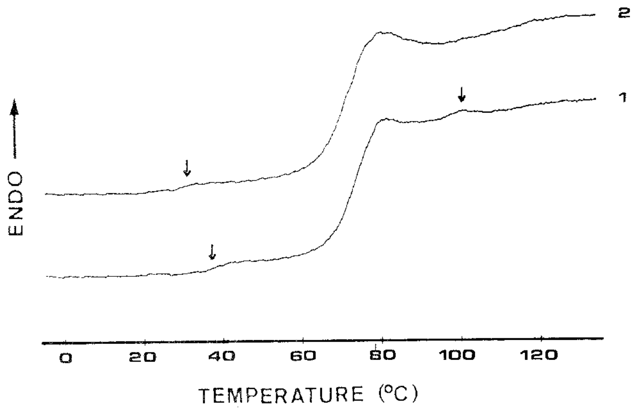


Figure 1 D.s.c. heating curves of the blends containing 10 wt% of (1) A2 and (2) B2, showing the phase separation in the blends

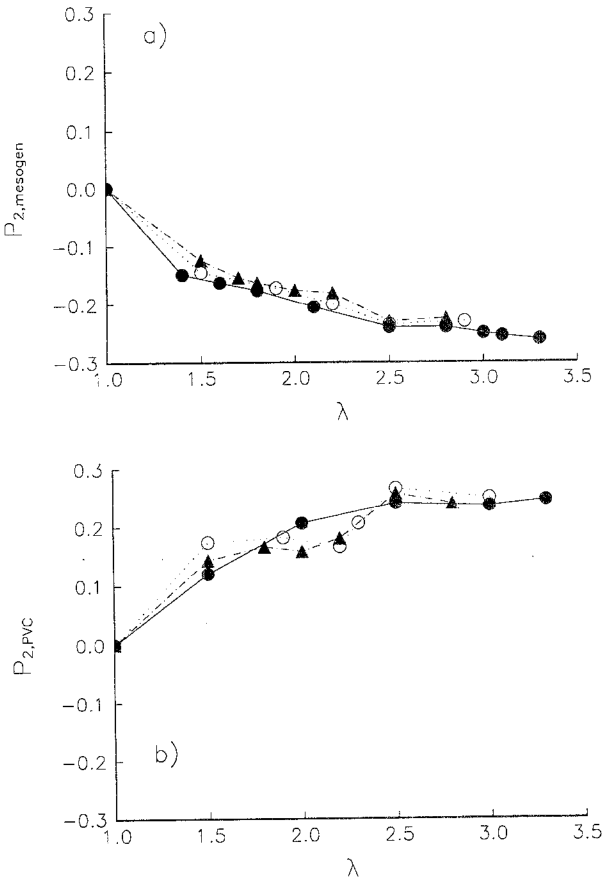


Figure 2 Order parameter of (a) the mesogenic groups and (b) the PVC matrix *versus* draw ratio for the blends containing the polymer and the ionomer samples in Series A: A1 (●), A2 (○) and A3 (▲). The blend samples were stretched at 80°C

blends with the series A samples, in spite of the low LCP concentration in the blends, an endothermic peak for the nematic to isotropic transition can be seen beyond the T_g region of PVC, but its position was found to shift to a lower temperature (about 5°C) as compared with the pure samples, which could be considered as an indication of the effect of the interfacial interactions between PVC and LCP. For the blends containing the series B samples, the transition peak cannot be found. This suggests a greater effect of the interfacial interactions in those blends.

Before discussing the results regarding the orientation of the mesogenic groups upon stretching, it must be emphasized that in this study the measured draw ratio was for the macroscopic deformation of the blend films and, as a first approximation, the actual draw ratio of the LCP phase in the blends was assumed to be similar. As will be shown later, as the main parameter used to characterize the orientation behaviour was the maximum macroscopic orientation which was achieved at low deformations for all the samples, this assumption has no consequences on the discussion revealing the effects of the ionic aggregates.

First, let us look at the stress-induced orientation behaviour of the LCP samples containing a biphenyl moiety in the side group (series A). The orientation development in all blends upon stretching at 80°C is shown in *Figure 2*, where the order parameter P_2 is plotted *versus* draw ratio. From *Figure 2a* it is seen that the macroscopic orientation of the mesogenic groups is grown perpendicularly with respect to the stretching direction, as is revealed by the negative P_2 values. This is a phenomenon often observed for LCPs having an odd number of CH_2 units in the flexible spacer that links the mesogenic groups to the chain backbone, and it has ben attributed to a perpendicular coupling of the mesogenic groups with respect to the chain backbone, whose orientation should be parallel to the stretching direction[8]. Comparing the different blend samples, it is clear that the orientation in the ionomers, regardless of the ion content, is similar to that of the polymer containing no ionic groups; the orientation in all samples seems to increase continuously with the extension, and a maximum P_2 of about −0.26 is obtained relative to −0.5 in the case of a perfect perpendicular orientation of all the mesogenic groups. For comparison, the orientation of the PVC matrix in the stretched samples is shown in *Figure 2b*. Based on the positive P_2 values, this orientation is along the stretching direction, and no difference is notable between the blends. A perfect orientation in the stretching direction corresponds to $P_2 = 1$.

The influence of the stretching temperature on the obtained orientation was also studied. The results for the samples stretched at different temperatures to a draw ratio of 2.5 are presented in *Figure 3*. *Figure 3a* shows the plot of P_2 of the mesogenic groups *versus* the stretching temperature. By inspection of the data, it is evident that when the samples are stretched at $T < T_{ni}$, i.e. in the nematic state, the orientation remains almost unchanged for all the samples, while when the stretching experiments are carried out at $T > T_{ni}$ the achieved orientation drops drastically. As the samples have different T_{ni} depending on the ion content (*Table 1*), this feature is better illustrated in *Figure 3b*, where P_2 is plotted *versus* the stretching temperature normalized to T_{ni}, namely, the reduced temperature. Indeed, within the errors of the measurements, all data fall into a same curve, showing the drop of P_2 at the region where $T/T_{ni} = 1$. Although the LCP samples were blended with PVC, it was expected that their stress-induced orientation was essentially independent of the PVC matrix. This is consistent with *Figure 3c*, showing the PVC orientation at different stretching temperatures. The drop of the orientation of the mesogenic groups shows no consequence on the PVC orientation in all the blends, which is almost constant

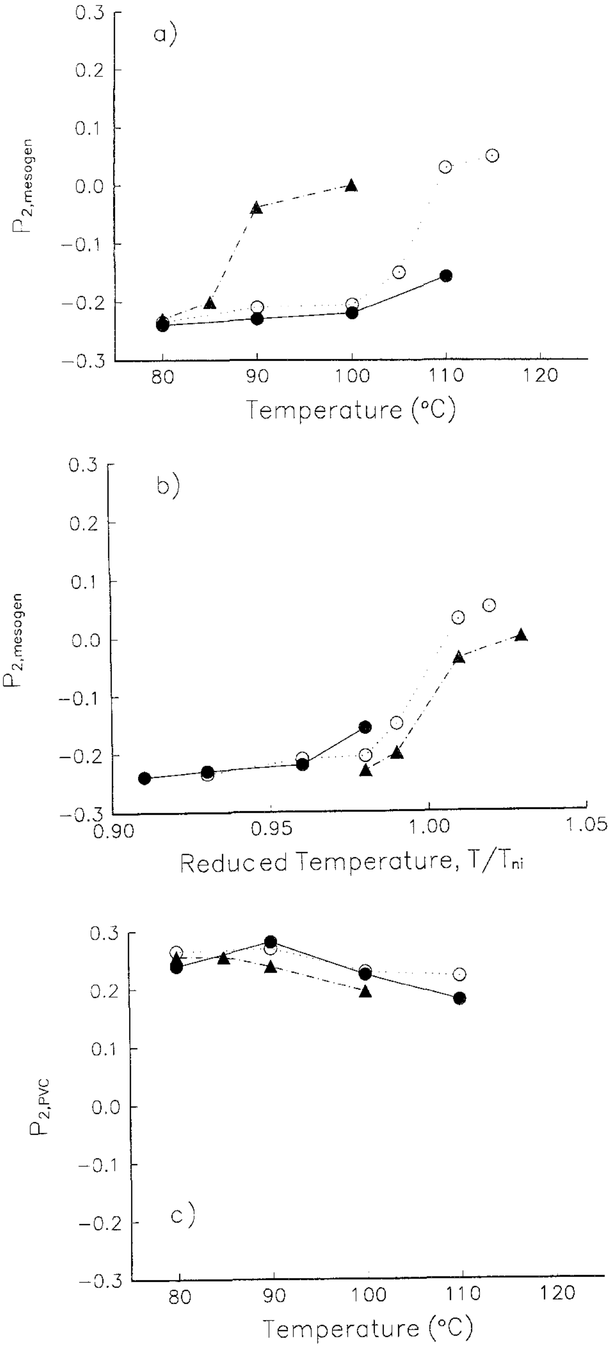


Figure 3 (a) Order parameter of the mesogenic groups *versus* stretching temperature, (b) order parameter of the mesogenic groups *versus* reduced stretching temperature, and (c) order parameter of the PVC matrix *versus* stretching temperature for the blends containing the polymer and the ionomer samples in series A: A1 (●), A2 (○) and A3 (▲). The blend samples were stretched to $\lambda = 2.5$

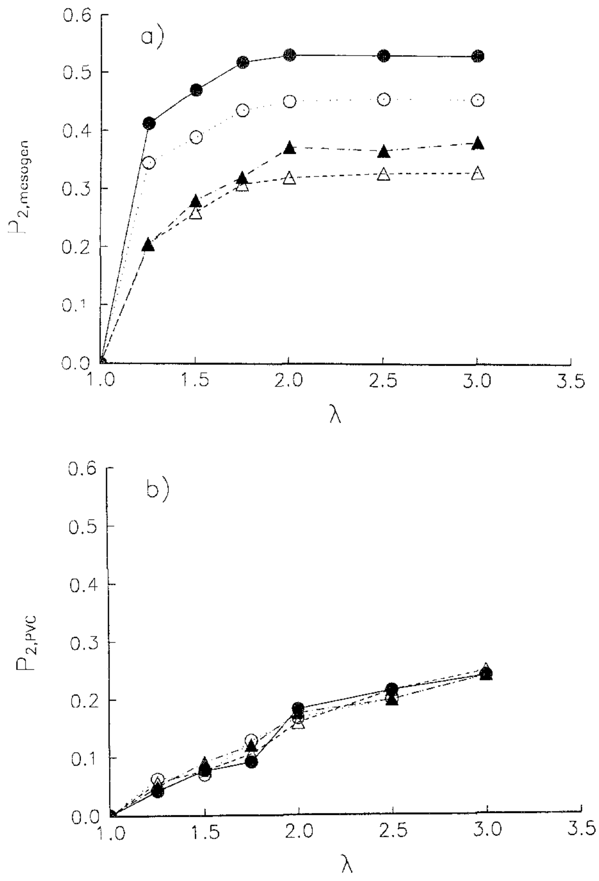


Figure 4 Order parameter of (a) the mesogenic groups and (b) the PVC matrix *versus* draw ratio for the blends containing the polymer and the ionomer samples in series B: B1 (●), B2 (○), B3 (▲) and B4 (△). The blend samples were stretched at 100°C

over the temperature range investigated. The results in *Figures 2* and *3* indicate that, for the series A samples, the ionic aggregates in the ionomers have no effects on the stress-induced macroscopic orientation of the mesogenic groups, which can only be achieved by applying a mechanical field to the samples in their nematic state.

For blends with LCP samples carrying a phenyl benzoate moiety in the side group (series B), the results for the stress-induced orientation are totally different. *Figure 4* shows the plots of P_2 *versus* draw ratio for the samples having different ion contents and stretched at 100°C. In contrast to the LCP samples of series A, the macroscopic orientation of the mesogenic groups, shown in *Figure 4a*, is parallel to the stretching direction. Moreover, in all cases P_2 rapidly attains a plateau value at a draw ratio of about 1.8. This plateau value can be considered as the achievable orientation upon stretching, which corresponds to a monodomain structure with a maximum alignment of the directors of the nematic domains. Therefore, it is evident that in these systems the ionic aggregates have a strong effect on the macroscopic orientation, since *Figure 4a* shows that the achievable orientation is systematically lowered as the ion content in the ionomer is higher. This result suggests that the ionic aggregates could reduce the nematic order characterizing the intrinsically oriented microstructure and, hence, lower the macroscopic orientation induced by external aligning fields. This is not unreasonable. An ionic aggregate is an association of several ion pairs, and the polymer chains which are anchored to the aggregates have a reduced number of available conformations; consequently the neighbouring mesogenic side groups could suffer from this effect and distort the local nematic order. On the other hand, from *Figure 4a*, the rate of the transition from a polydomain to a monodomain structure upon extension is not affected by the ionic aggregates. Also, once again, the orientation of the PVC matrix in these blends shows no difference, as can be seen in *Figure 4b*, and it is much lower than that of the mesogenic groups.

More interestingly, the achievable orientation was

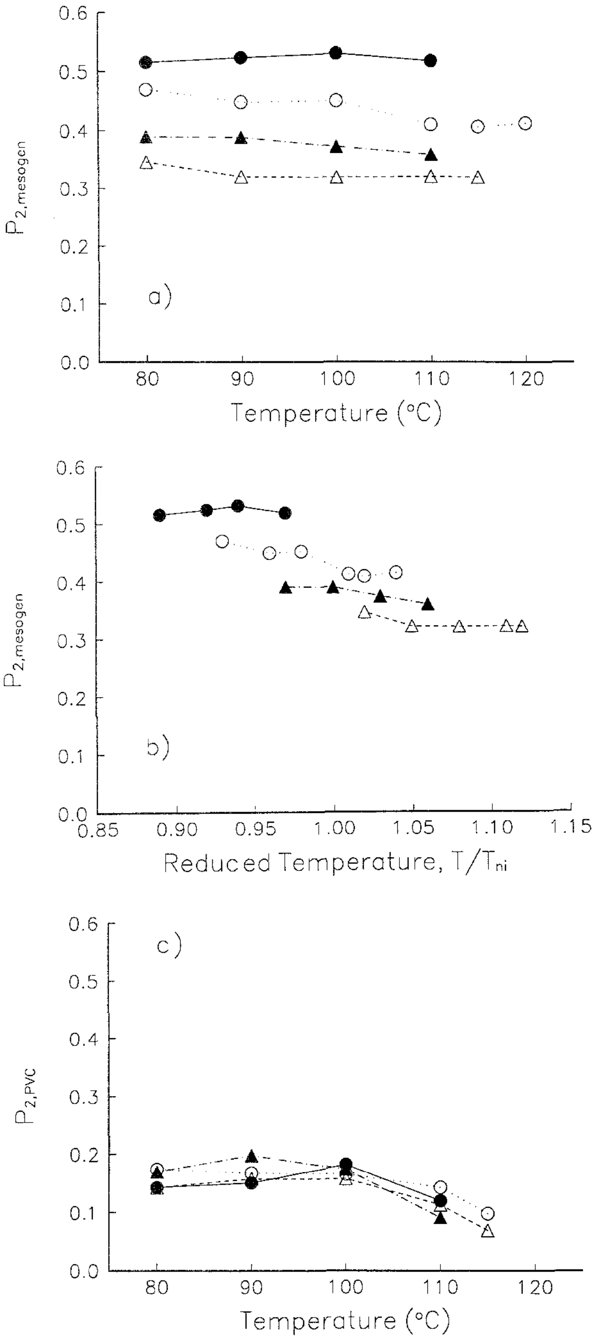


Figure 5 (a) Order parameter of the mesogenic groups *versus* stretching temperature, (b) order parameter of the mesogenic groups *versus* reduced stretching temperature, and (c) order parameter of the PVC matrix *versus* stretching temperature for the blends containing the polymer and the ionomer samples in series B: B1 (●), B2 (○), B3 (▲) and B4 (△). The blend samples were stretched to $\lambda = 2$

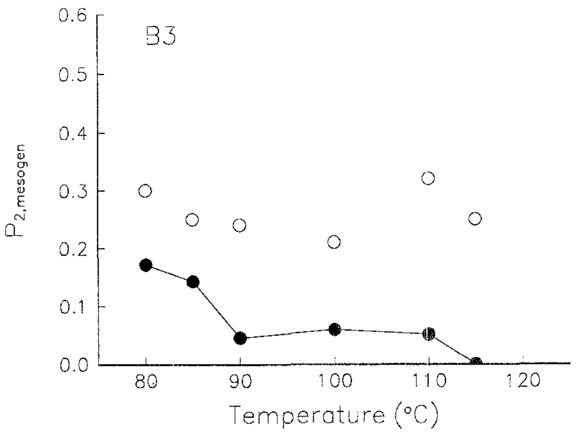


Figure 6 Order parameter of the mesogenic groups *versus* stretching temperature for the blend containing B3, stretched to $\lambda = 2$. The orientation measurements were made: immediately following stretching with the sample held at the stretching temperature (●); and after cooling under strain of the sample to room temperature (○)

determined at different stretching temperatures, and the results are given in *Figure 5*. *Figure 5a* shows that lowering of the orientation of the mesogenic groups is observed at all temperatures and the orientation for each sample is almost independent of the stretching temperature, and no drop of the orientation occurs over the entire temperature range investigated. As the samples have different T_{ni} (*Table 1*), *Figure 5b* also shows the orientation results expressed by plotting P_2 *versus* T/T_{ni}. Here it should be mentioned that the range of stretching temperatures was limited by the fact that the films broke when stretched at lower or higher temperatures. It can be seen in *Figure 5b* that for B1, the polymer containing no ionic groups, all the stretching temperatures are below its T_{ni}, i.e. $T/T_{ni} < 1$, while for two of the ionomers, B2 and B3, the temperatures cover both the nematic and the isotropic state, and for B4, which has the lowest T_{ni}, all the temperatures are above its T_{ni}. Surprisingly, even though the samples were stretched in the isotropic state, almost the same achievable orientation was obtained as when they were stretched in the nematic state. This behaviour is clear for B2 and B3 and, based on the whole of the results in *Figures 4* and *5*, should be expected for B1 and B4. This is an interesting and unexpected result, and contradicts the general finding revealed in *Figure 3* as well as in our previous studies[6,7]; that is, if a nematic polymer is stretched (or deformed) in the isotropic state, the absence of the nematic domains, which means the absence of cooperative effects, results in no macroscopic orientation of the mesogenic groups. Before discussing this phenomenon it can be noted, from *Figure 5c*, that the PVC matrix in all blends shows a similar orientation. The decrease in its orientation level at the higher stretching temperatures arises from a more important chain relaxation.

The underlying orientation mechanisms which lead to this observed macroscopic orientation at stretching temperatures above T_{ni} have been investigated. *Figure 6* shows the results of a series of experiments conducted on B3, the ionomer having a T_{ni} at about 90°C. Using a stretching apparatus placed in a temperature-controlling unit designed for making polarized infra-red measurements at high temperatures, the B3 blend films were stretched to a draw ratio of 2 at different temperatures. For each film, instead of quenching it immediately after the stretching, the orientation measurements were performed (the required time was about 8 min); then it was cooled under strain to room temperature and the orientation was determined once again. As can be seen from *Figure 6*, when the film was stretched at $T < T_{ni}$ the stretching did result in a macroscopic orientation of the mesogenic groups, while at $T > T_{ni}$ there was only a slight orientation, and when the film was stretched at 115°C there was no orientation at all. But, following cooling under strain at room temperature, a uniform

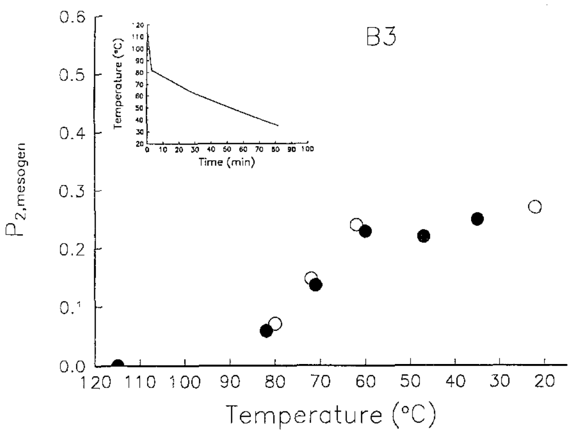


Figure 7 Order parameter of the mesogenic groups *versus* temperature for the blend containing B3, stretched to $\lambda = 2$ at 115°C and then allowed to cool under strain (●). The sample was then reheated to 115°C and recooled under strain (○). The cooling curve of the oven is shown, indicating a cooling rate of $\sim 0.6°\text{C min}^{-1}$

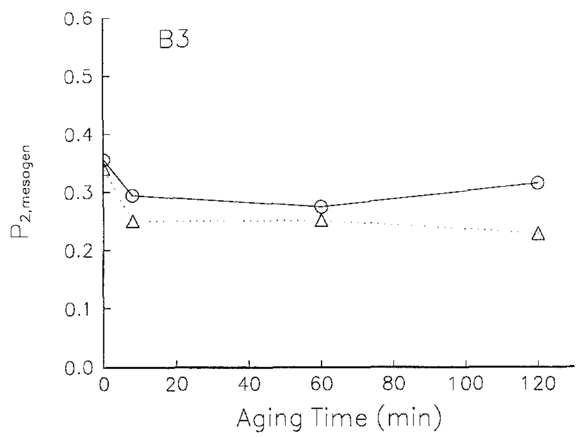


Figure 8 Order parameter of the mesogenic groups *versus* ageing time for the blend containing B3, stretched to $\lambda = 2$ at 80°C (○) and 115°C (△), and held at these temperatures for different lengths of time before quenching at room temperature

macroscopic orientation was obtained for all the stretching temperatures. This result clearly indicates that, for this particular blend system, the main effect of the cooling process is not, as has been believed, to preserve the macroscopic orientation induced by the stretching, but to induce or complete this orientation. With the stretching temperatures below T_{ni}, the orientation arising from the stretching is enhanced during cooling, while at $T > T_{\text{ni}}$ almost the whole orientation takes place during cooling. We have further examined this phenomenon by doing other experiments. *Figure 7* shows the orientation development during the cooling process under strain. For this experiment, a B3 film was stretched at 115°C to $\lambda = 2$, and the measurements showed no orientation; then the film was allowed to cool by opening the cover of the oven, and subsequent orientation measurements were made at different temperatures. As indicated by the cooling curve of the oven, which is also given in *Figure 7*, the temperature dropped rapidly to about 82°C after the first 3 min, and then fell at almost a constant rate ($\sim 0.6°\text{C min}^{-1}$). Taking into account a probable gap of several degrees between the indicated temperature of the oven and the sample temperature, it is clear that macroscopic orientation started to develop, apparently linearly, once the sample passed from the isotropic state into the nematic state; it reached a plateau value at about 60°C and remained constant at lower temperatures. Moreover, as also shown in *Figure 7*, this orientation process was totally reversible. When the film was reheated to 115°C, the orientation was lost, and by cooling under the same conditions the same orientation growth was found.

There are two possible mechanisms responsible for the above results. A stretched film cooled under strain means that it is under the effect of a mechanical force that sustains the extension of the film. As a consequence, the nematic domains formed while the LCP sample is cooled to $T < T_{\text{ni}}$ could have a quick response to the stress field by alignment along the field direction. For the blends studied here, it is reasonable to say that most of the mechanical force is related to the extension (orientation) of the PVC matrix (90% by weight), and basically this field is effective to the stretched film until the PVC chains are completely immobilized at temperatures below its T_g. If this is the case, the interfacial interactions between the phases of both polymers could play a determining role in the transfer of the stress field to the LCP sample, which is necessary for the alignment. We have carried out some experiments aimed at verifying this mechanism. *Figure 8* shows the results of the orientation of the B3 films quenched at room temperature after being stretched at 80°C and 115°C to $\lambda = 2$ and, before quenching, held at these temperatures for different lengths of time. It was expected that the orientation relaxation of the PVC matrix could take place and thus reduce the mechanical force acting on the stretched film before cooling. Although it seems that the samples immediately quenched after stretching (with the least PVC relaxation before quenching) show the highest level of orientation, a clear assessment about the effect of the matrix polymer's relaxation cannot be made, since the samples relaxed for different times have a similar orientation after cooling. This can be due to the fact that the orientation relaxation of the PVC at these temperatures is slow, in other words, the lowering of the stress field is not significant. Actually, even if the stress field is much diminished it can still be sufficient to initiate the alignment of the nematic domains once the LCP samples enter into their liquid crystalline state.

The other possibility is an important role of the orientation of the LCP chain backbone in the orientation of the mesogenic groups during cooling. The chain backbone of the LCP sample should be expected to align during stretching along the field direction. This means an anisotropic environment for the mesogenic groups in the isotropic state, and once the nematic order is reformed among them during cooling, the nematic domain directors could tend to follow this anisotropy and to align, owing to the coupling between the mesogenic groups and the chain backbone. Unfortunately, in the present study, because of the overlapping of the infra-red bands we could not determine the orientation of the chain backbone in order to gain a closer insight into its relation to the orientation of the mesogenic groups during cooling. However, based on some previous investigations[6,7,9], the orientation of the chain backbone

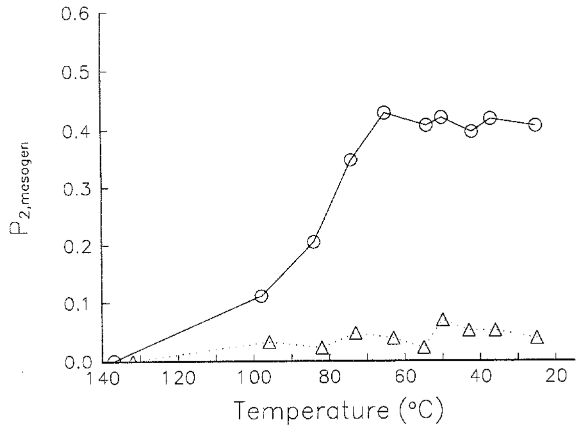


Figure 9 Order parameter of the mesogenic groups *versus* temperature for the poly(methyl methacrylate) blends containing A1 (Δ) and B1 (O), stretched to $\lambda = 2$ at $T_{ni} + 15°C$ and then allowed to cool under strain. The cooling curve is similar to that shown in *Figure 7*

could be expected to be very low as compared with the orientation of the mesogenic groups.

Now, as the films of the blend containing the initial polymer B1 could not be stretched at $T > T_{ni}$, the question that can be asked is whether this orientation development during cooling under strain is a property related to the ionic aggregates in the ionomers. We conducted some experiments to answer this question. A poly(methyl methacrylate) sample, whose T_g ($\sim$ 110°C) is higher than that of PVC, was utilized as the matrix, which allowed the blend samples to be stretched at higher temperatures. Two blends, containing 10 wt% of the initial polymers, B1 and A1, respectively, were prepared for the experiments. The films were stretched at $T_{ni} + 15°C$, i.e. 137°C for the B1 blend and 132°C for the A1 blend, and then allowed to cool under strain, under the same conditions described for the experiment of *Figure 7*, while the orientation measurements were made at different temperatures. It can be seen in *Figure 9* that in both cases no orientation of the mesogenic groups was achieved after stretching, and as the samples were cooled onto the liquid crystalline state a macroscopic orientation along the stretching direction was induced for B1, as occurred for its ionomers (*Figure 7*), while for A1 no macroscopic orientation perpendicular to the stretching direction was observed, as for its blend with PVC as matrix. However, it is interesting to notice that a slight parallel orientation can be seen. These results, obtained with a different polymer matrix, confirm that the orientation induction during cooling under strain is characteristic for B1, and does not result from the presence of the ionic aggregates.

The fact that this macroscopic orientation of the mesogenic groups that occurred during cooling and under strain cannot be observed for every LCP sample in the blend, like those of series A, must be attributed to their differences in the factors discussed above. As has been mentioned, the d.s.c. measurements seem to indicate stronger interfacial interactions in the blends containing the samples of series B, which is consistent with the observed orientation behaviour. Choosing appropriate polymer matrices, further investigations are being undertaken in our laboratory to better understand this phenomenon in terms of those factors, i.e. interfacial interactions between both polymers, stress field transfer to or build-up on the LCP phase, orientation relaxation of the matrix polymer, orientation of LCP chain backbone in the blend, and nature and magnitude of the coupling between the mesogenic groups and the chain backbone.

CONCLUSION

The stress-induced macroscopic orientation of the mesogenic groups in two series of side-chain LC ionomers was studied and compared to the corresponding polymers containing no ionic groups. The investigations were made possible by blending the LCP samples with an immiscible PVC matrix and stretching the blend films. Very distinct orientation behaviours were found for the LCP samples having different mesogenic units in the side group. For the ionomers prepared from a polyacrylate bearing a biphenyl moiety in the side group (series A), their orientation behaviour, regardless of the ion content, was found to be similar to that of the initial polymer: the orientation develops in the same manner with extension, the achievable orientation is of the same magnitude, and the macroscopic orientation can be induced only by stretching the sample in the nematic state. In contrast, for the ionomers based on a polyacrylate carrying a phenyl benzoate moiety in the side group, the ionic aggregates display profound effects on the macroscopic orientation of the mesogenic groups; the level of the achievable orientation is systematically lowered as the ion content in the ionomer is higher. This suggests a reduced nematic order, i.e. a less oriented microstructure in these ionomers. More interestingly, it was found that the stress-induced orientation was almost constant when the blend films were stretched either in the nematic state or in the isotropic state. Studying the underlying orientation mechanisms, it was found that the observed macroscopic orientation was achieved mainly during the cooling of the samples under strain. Our results show that when the sample is stretched at $T < T_{ni}$, only a partial orientation of the mesogenic groups is induced and this orientation is improved during the cooling process; however, when the sample is stretched at $T > T_{ni}$, little or no orientation is induced by stretching, and cooling of the sample under strain into the nematic state is accompanied by the appearance of macroscopic orientation. The interfacial interactions between the phases of both polymers, which could be important for the stress field transfer to or build-up on the LCP component, as well as the orientation of the LCP backbone in the blends, are suggested as being among the factors which can affect this orientation process during cooling and under strain.

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