A polarized infra-red spectroscopic study of mechanically induced orientation in side-chain liquid crystalline polymers

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We exploit the utility of infra-red dichroism for studying the orientation in thin films of side-chain liquid crystalline polymers (LCPs). Mechanical stretching of these polymers is difficult to perform because of difficulties in preparing the actual film samples necessary for the experiments. The method we used in this study consists of casting a thin LCP film onto the surface of a supporting conventional polymer film which can easily be prepared and stretched over a wide temperature range. Three nematic polyacrylates were investigated in this way, using poly(vinyl alcohol) as the supporting polymer. It is shown that stretching of the LCP film is sustained by extension of the supporting film and, similar to cross-linked nematic elastomers, an order parameter of approximately 0.4 for the mesogenic groups, determined by infra-red dichroism measurements, is obtained at a draw ratio as small as 1.5, i.e. only 50% deformation, indicating a rapid macroscopic alignment of the nematic domains along the mechanical field direction. Comparisons show that the mechanical stretching is particularly efficient for obtaining high orientation in side-chain LCPs having a short flexible spacer, the orientation of which is difficult to develop in a magnetic field, revealing an opposite influence of the length of the flexible spacer on the alignment of the nematic domains in both magnetic and mechanical fields. The mechanism of the orientation process in this stretching method is also examined. It is proposed that the stress field is essentially transferred to the nematic polymer through the interface between the nematic and supporting films, and that the alignment of the nematic domains, which starts in the interfacial region, could propagate throughout the sample by virtue of a strong cooperative movement among the nematic domains. The efficiency of the alignment propagation is higher for LCPs containing a short flexible spacer because of the stronger couplings between the chain backbone and the mesogenic groups.

(Keywords: liquid crystalline polymers; orientation; infra-red dichroism)

INTRODUCTION

A macroscopic and uniform alignment of the mesogenic groups is of major importance for the potential applications of side-chain liquid crystalline polymers (LCPs). Now, it is well known that this orientation can be generated by magnetic, electric, surface, or mechanical field effects[1,2] and can then be preserved by simply cooling the polymer below its glass transition temperature (T_g). Examining the application of an extensional force, which obviously is a convenient method for orienting the mesogenic groups in thin LCP films, the main problem arises from the difficulty of preparing the appropriate samples needed for the drawing experiments.

We believe that this is, at least partly, the reason for which only two methods were reported in the literature for obtaining mechanically induced orientation in side-chain LCPs. The first method is fibre drawing from the isotropic state, i.e. at temperatures well above the nematic to isotropic transition temperature (the clearing temperature, T_{cl}) and hence there are no nematic domains during the orientation process. An orientation of the mesogenic groups, either parallel or perpendicular to the stretching direction, depending on the structure of the polymer, was observed by X-ray scattering measurements[3]. The second method is based on preparing a nematic elastomer by introducing a number of chemical cross-links, which enhances the polymer orientability and facilitates the stretching experiment. It is recognized that these nematic elastomers are of great interest and a molecular switching (a rapid macroscopic orientation of the mesogenic groups) can readily be achieved by drawing the polymers in their liquid crystalline state[4–6]. Nevertheless, this approach does have some drawbacks. For example, the presence of the chemical units used to crosslink the polymer generally reduces the range of the mesophase (the temperature range between T_g and T_{cl})[6], and the macroscopic orientation is lost when the mechanical field is removed at temperatures above T_g.

In this paper, we describe a simple drawing method which allows us to effectively obtain a macroscopic orientation in the side-chain LCPs and to use the infra-red dichroism technique to study the orientation behaviour. The method is based on casting a thin nematic LCP film onto the surface of a pre-prepared conventional polymer film which can readily be stretched at temperatures between T_g and T_{cl} of the nematic polymer. The utilization of such a supporting film was initially proposed for

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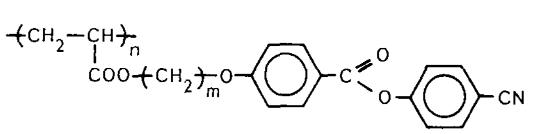
making it possible to use infra-red dichroism to study the time-dependent orientation in a thin nematic polymer film induced by a magnetic field[7]. Obviously, it is also fairly well suited to orientation measurements on thin stretched films. As will be shown in this paper, the method is highly efficient for inducing the orientation; the stretching of the nematic polymer is sustained by extension of the supporting film and a rapid macroscopic alignment of the nematic domains, when stretched in the liquid crystalline state, leads to a high orientation of the mesogenic groups.

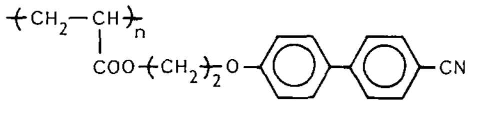
EXPERIMENTAL

Samples

Three nematic polyacrylates, referred to as PA2, PA6, and BiPA2, were investigated in this study. PA2 and PA6 have the following structure:



with $m=2$ and 6 for PA2 and PA6, respectively. They differ only in the length of the flexible spacer (the alkyl chain) which connects the mesogenic group to the polymer main chain (backbone). The polyacrylate BiPA2 differs from PA2 and PA6 by its mesogenic group, and has the following structure:



The syntheses of these polymers have been carried out using the methods described in the literature[8,9], with the characteristics of the materials being given in *Table 1*. The molecular weights were estimated by g.p.c. using polystyrene standards. The phase behaviour was measured with a differential scanning calorimeter (Perkin–Elmer DSC-7), using a heating rate of 20°C min^{-1} and a sample weight of ~15 mg. As reported in the literature, all three LCPs exhibit only a nematic mesophase characterized by a nematic to isotropic transition temperature T_{cl}.

In the preparation of the film samples used for the stretching experiments, the LCP solution should first be cast onto the surface of the supporting film to form a thin nematic polymer film, before removing the solvent. Therefore, three basic conditions should be fulfilled for a supporting film: (i) it can be stretched at temperatures corresponding to the liquid crystalline state of the nematic polymer; (ii) the solvent used for the nematic polymer solution should not dissolve the supporting film, and (iii) the infra-red absorption bands of the supporting film do not overlap the infra-red bands of the nematic polymer used for the dichroism measurements. The supporting, conventional polymer used in this study is a 99%-hydrolysed poly(vinyl alcohol) (PVA) purchased from Aldrich (having a molecular weight of ~150 000 g mol^{-1}). This is a crystalline polymer having a very good deformability and can easily be drawn over a wide temperature range, from room temperature up to its melting point (~220°C), which covers the temperatures between T_g and T_{cl} of the three nematic polyacrylates.

Table 1 Characteristics of the nematic polyacrylates

Polymer	T_g (°C)	T_{cl} (°C)	M_n	M_w/M_n
PA2	75	105	34 000	1.47
PA6	33	125	56 000	2.7
BiPA2	79	113	86 900	1.72

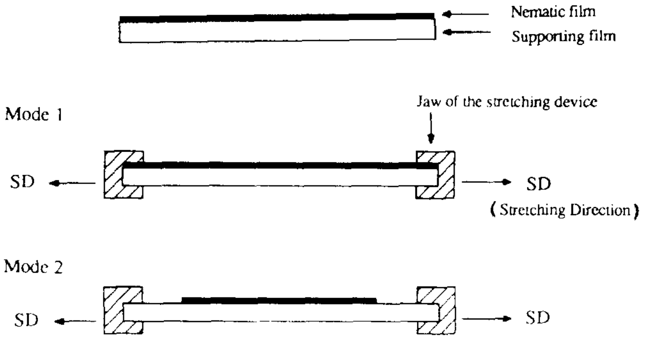


Figure 1 Schematic representation of the drawing experiments. In mode 1, both the nematic and the supporting films are clamped by the jaws of the stretching device, while in mode 2, only the supporting film is clamped

The following procedure is used to prepare the film samples. A PVA film was first obtained by casting a 12 wt% aqueous solution onto the surface of a glass plate, with the mixture being heated to 80°C to achieve a clear solution before casting. This film (~100 μm thick) was dried under vacuum at 80°C for 2 days. A thin nematic polyacrylate film was then cast from a 10 wt% THF solution onto the surface of the dry PVA film, and then dried under vacuum at 50°C for several days. THF is a non-solvent for PVA. In general, the thickness of the nematic film was controlled so as to be of the order of 20 μm.

Mechanical drawing experiments were performed on a hand-driven apparatus which had been constructed in our laboratory. In a typical experiment, this stretching device was placed in an oven with a well controlled temperature, and the stretching of the film (16 mm in length and 6 mm in width before stretching) was achieved by a simultaneous extension of two jaws clamping both ends of the film. The drawing rate was ~50 mm min^{-1}, and had no influence on the orientation that was obtained. For the orientation measurements, the film was cooled at room temperature immediately following the stretching process. No retraction of the stretched samples was observed. Small ink marks were traced on the surface of the nematic polymer film in order to accurately determine the draw ratio, λ (defined as $\lambda = l/l_0$, with l_0 and l being the film length before and after the stretching, respectively).

By changing the casting area of the nematic polymer on the surface of the PVA film, as illustrated schematically in *Figure 1*, the samples were stretched in two different ways, with either both nematic and PVA films clamped by the jaws of the stretching apparatus (mode 1) or with only the PVA film clamped (mode 2). Similar results on orientation were obtained in the two cases, suggesting that essentially the PVA film sustains the extensional force and transfers the stress field to the LCP film. Unless otherwise stated, the results shown in this paper are those obtained with the drawing experiments performed using the mode 1 arrangement.

Orientation measurement

The infra-red dichroism technique is particularly convenient for orientation measurements in thin nematic polymer films. It allows one to determine the order parameter P_2, which is defined as $P_2=(3\langle\cos^2\theta\rangle-1)/2$, in which θ is the angle between the stretching direction (SD) and either the long axis of the mesogenic group (for orientation of the mesogenic group) or the main chain axis (for orientation of the polymer backbone). The order parameter is a measure of the average orientation over all molecular units being studied (mesogenic groups or chain segments), and ranges from 0, for the random orientation, to 1, for the perfect orientation parallel to the SD. P_2 is related to the infra-red dichroism by $P_2=(R_0+2)(R-1)/(R_0-1)(R+2)$, in which R is the infra-red dichroic ratio and is defined as $R=A_{\parallel}/A_{\perp}$ ($A_{\parallel}$ and $A_{\perp}$ being the measured absorbances with the infra-red beam polarized parallel and perpendicular, respectively, to the SD), and R_0 is given by $R_0=2\cot^2\alpha$, where α is the angle between the axis of the mesogenic group (or the chain segment) and the transition moment associated with the infra-red band used for the dichroism measurements.

Figure 2 shows the infra-red spectra, in the 1460–2560 cm^{-1} region, of PA2, BiPA2, and PVA. The C≡N end group in the three nematic polyacrylates exhibits the characteristic stretching vibration band at 2230 cm^{-1} which is well suited to the P_2 measurement of the mesogenic groups[5,7,10]; PVA has no absorption band in this vicinity. By defining the long molecular axis as the line connecting the centres of the two phenyl rings, the angle α is $\sim 11^{\circ}$[11] for PA2 and PA6, and is obviously 0° for BiPA2. It follows that P_2 of the mesogenic groups can be calculated from $P_2=1.06(R-1)/(R+2)$ for PA2 and PA6, and $P_2=(R-1)/(R+2)$ for BiPA2.

It is interesting to be able to observe simultaneously the orientation of the mesogenic group and that of the polymer main chain. According to the spectra shown in *Figure 2*, the carbonyl stretching band near 1734 cm^{-1} is also not overlapped by any PVA bands. However, the situation is complicated for PA2 (and PA6) since this band arises from two carbonyl groups, with one linked to the chain backbone while the other one is part of the mesogenic group. As for BiPA2, there is only one carbonyl group attached to the chain backbone. The C=O band was used to estimate the orientation of the polymer main chain for BiPA2. By defining the chain axis as the line connecting two adjacent CH$_2$ units, the angle α is known to be $\sim 78^{\circ}$[12]. In this case, we have $P_2=-2.3(R-1)/(R+2)$. The difference between PA2 and BiPA2 in the number of carbonyl groups can be seen from the much more important absorption at 1734 cm^{-1} for PA2, with respect to the C≡N band at 2230 cm^{-1}.

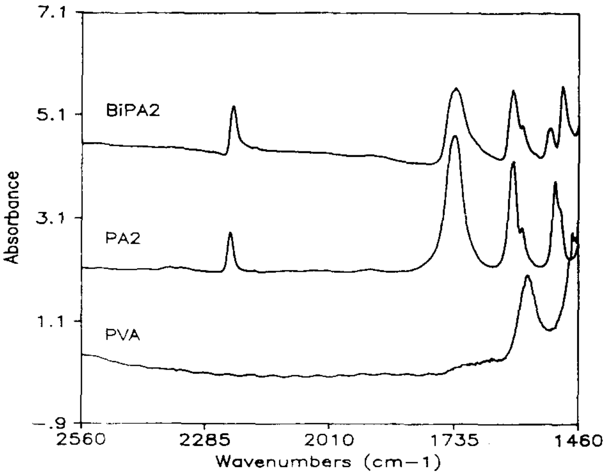


Figure 2 Infra-red spectra, in the 1460–2560 cm^{-1} region, of the two nematic polyacrylates, PA2 and BiPA2, and the supporting polymer PVA

For infra-red dichroism measurements, the polarized infra-red spectra were recorded on a BOMEN MB-102 Fourier transform infra-red spectrometer, at a resolution of 4 cm^{-1} and from a total of 50 interferograms for each spectrum. Polarization of the infra-red beam was obtained by a wire-grid polarizer placed between the film and the DTGS detector.

RESULTS AND DISCUSSION

Before presenting the results that have been obtained, it should be mentioned that the surface of the supporting PVA films has not been treated in any specific way to promote the well known surface effects-induced macroscopic orientation of the mesogenic groups. The dichroism measurements on non-stretched film samples placed at different temperatures between T_g and T_{cl} over time-periods up to 1 h showed no preferential orientation along any directions. Therefore, it is ensured that the orientation observed in this study did result from the drawing of the samples.

The stress-induced orientations in the three nematic polyacrylates with similar film thicknesses are depicted in *Figure 3*, where the order parameter P_2 is plotted as a function of the draw ratio λ. It can be seen that, similar to the results observed for cross-linked nematic elastomers, the orientation of the mesogenic groups increases drastically upon stretching. This is most clearly illustrated by the behaviour of PA2 (see *Figure 3a*). In this case, P_2 reaches a value of ~ 0.4 at a draw ratio as small as 1.5 and then attains a plateau value of ~ 0.5 after $\lambda=2$. The behaviour of BiPA2 is similar, while the orientation in PA6 increases less efficiently with stretching and the maximum of P_2 is smaller when compared to both PA2 and BiPA2. On the other hand, *Figure 3* also gives the results obtained for PA2 and PA6 with two different stretching temperatures, namely 85 and 102°C. It is obvious that there is little effect on the orientation of the mesogenic groups, contrary to the strong temperature dependence generally observed for the chain orientation in conventional polymers. In the case of BiPA2, only one stretching temperature was used, and what is also shown in *Figure 3c* is the orientation of the chain backbone, which is much smaller than that of the mesogenic groups but follows a similar development upon stretching, with a maximum P_2 of ~ 0.15 after $\lambda=2$. It should be noted that this P_2 value is consistent with those reported in the literature[13] for the orientation of the chain backbone in side-chain LCPs which are induced by a magnetic field and measured by ^{2}H n.m.r. spectroscopy.

In *Figure 4*, the plateau P_2 value (maximum orientation) of the mesogenic groups in the three nematic polymers,

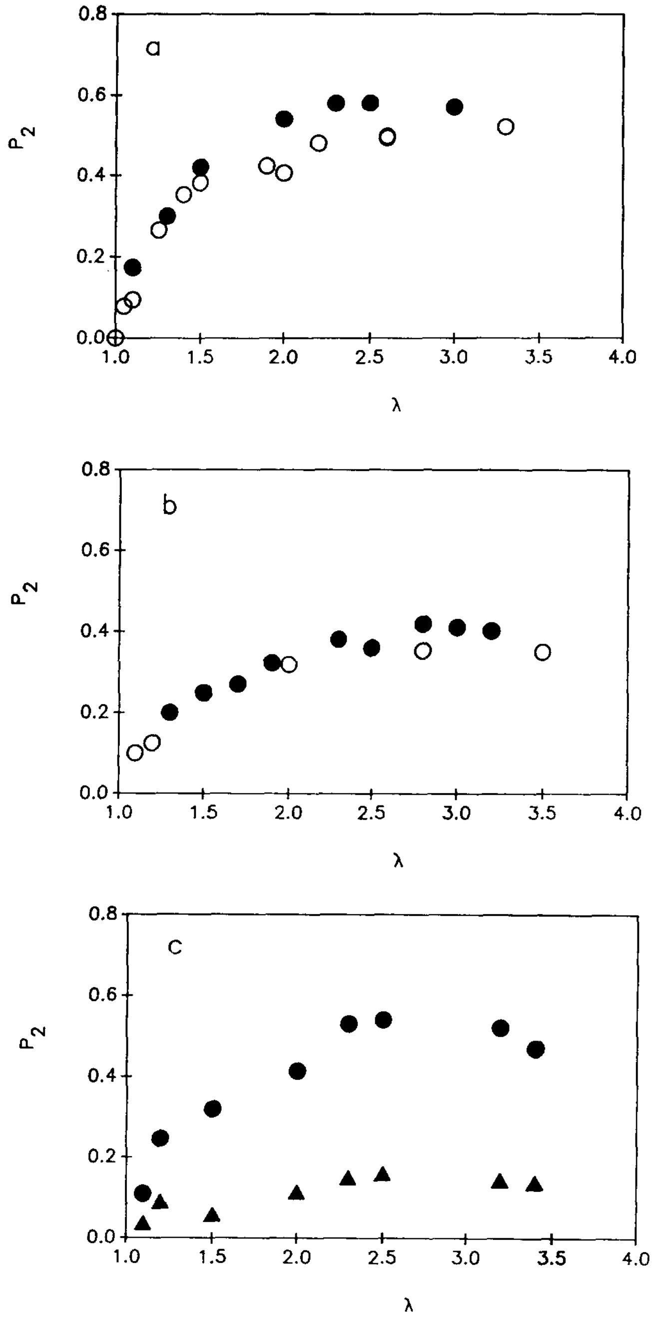


Figure 3 Order parameter as a function of draw ratio for: (a) PA2 stretched at 85°C (●) and 102°C (○); (b) PA6 stretched at 85°C (●) and 102°C (○); (c) BiPA2 stretched at 85°C, showing results obtained for the mesogenic group (●), and the main chain backbone (▲)

obtained at $\lambda > 2$, is shown as a function of the stretching temperature ($T > T_g$). The main chain orientation is also given in the case of BiPA2. For comparison, the same figure also shows the orientation in the same film samples of both PA2 and PA6 when placed in a 5.9 T-magnetic field at different temperatures for 1 h (see ref. 7 for experimental details). The following observations can be made concerning these results.

First, the orientation of the mesogenic groups is almost constant over the entire stretching temperature range between T_g and T_{cl}. However, with the temperature approaching the nematic to isotropic transition, this attainable orientation starts to decrease and drops to zero when the stretching experiment is performed at temperatures above T_{cl}. These results, combined with those shown in *Figure 3*, clearly indicate that, similar to the magnetic field-induced orientation, the observed orientation of the mesogenic groups is governed by the macroscopic alignment of the nematic domains in which the mesogenic groups are preferentially oriented along a local director. Since the alignment can only take place in the liquid crystalline state, when the sample is stretched in the isotropic state ($T > T_{cl}$) the absence of the nematic domains does not give rise to any orientation of the mesogenic groups.

Secondly, the comparison between the mechanical and magnetic orientations show that the drawing method is highly effective for PA2. For most temperatures, the

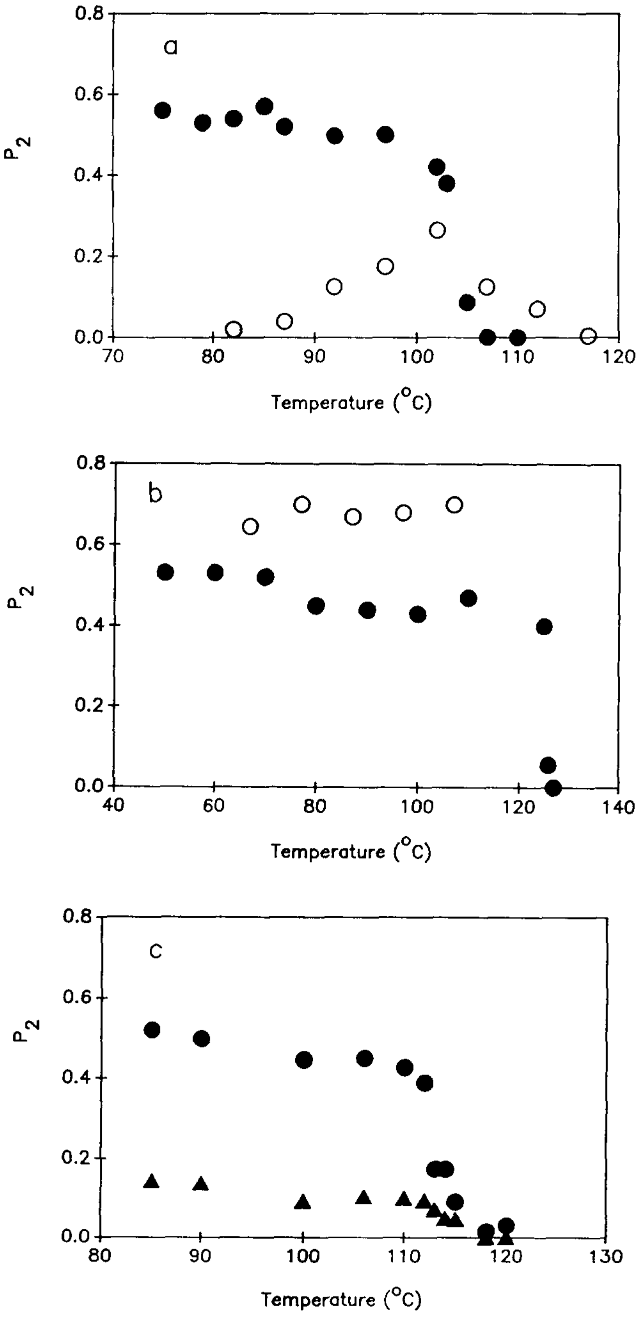


Figure 4 Order parameter as a function of orientation temperature for: (a) PA2, with mechanical stretching (●), and with application of a magnetic field (○); (b) PA6, with mechanical stretching (●), and with application of a magnetic field (○); (c) BiPA2, with mechanical stretching, showing results obtained for the mesogenic group (●), and the main chain backbone (▲)

mechanically induced orientation is much greater than the magnetic field-induced orientation, which apparently has a maximum P_2 at ~102°C. The difference is particularly striking at temperatures near the T_g of the polymer. On the basis of the local order parameters obtained for typical side-chain LCPs[1], the P_2 at ~0.5 for PA2 indicates an almost perfect alignment of the directors of the nematic domains along the stretching direction. However, as far as PA6 is concerned, and in contrast to PA2, the magnetic field effects are more efficient than the mechanical stretching approach. Its magnetic orientation is revealed by a P_2 of ~0.7, which is greater than the stress-induced orientation.

The difference in the orientation behaviour between PA2 and PA6 results from the difference in length of the flexible spacer group. The results shown in *Figure 4* suggest an opposite role of the flexible spacer in the mechanically induced alignment of the nematic domains with respect to the alignment induced by a magnetic field. A shorter spacer group in PA2 gives rise to a stronger coupling between the mesogenic groups and the chain backbone, when compared to PA6 which contains a longer spacer group. In a magnetic field, the magnetic forces operate directly on the nematic domains to cause their alignment; a strong coupling hinders the alignment and, hence, the orientation. The situation is different when a nematic polymer is subjected to a mechanical field. The mechanical forces couple to the polymer chains, and a stronger coupling between the main chain and the mesogenic groups results in a stronger effect (more transfer) of the mechanical field on the nematic domains, thus leading to more alignment.

In addition, the results for BiPA2 shown in *Figure 4c* include the maximum orientations of both the mesogenic groups and the main chain. It can be seen that the main chain orientation changes with the stretching temperature in a similar way when compared to the orientation of the mesogenic groups. Both orientations fall to zero at $T > T_{cl}$. Taken together with the results in *Figure 3*, it seems likely that the observed main chain orientation is essentially imposed by the high orientation of the mesogenic groups, due to significant couplings in this nematic polymer which also has a short flexible spacer group. On the other hand, it is worthwhile to note that there is no noticeable difference in the stress-induced orientation between BiPA2 and PA2, which differ in their mesogenic groups.

Now, in order to obtain more information on the mechanism of the orientation process in this present drawing method, we investigated the influence of the thickness of the nematic polymer film. Films of PA2 and PA6 with different thicknesses were specifically cast onto the surface of the PVA film, and the stretching experiments were carried out by clamping only the PVA film (mode 2 in *Figure 1*). The samples were stretched at temperatures of 3°C below the T_{cl}, i.e. at 102°C for PA2, and at 122°C for PA6, and their thicknesses were measured, in terms of the infra-red absorption at the 2230 cm^{-1} band, by $(A_{\parallel} + 2A_{\perp})/3$, which is proportional to the thickness. The results are shown in *Figure 5* where the maximum orientation is plotted as a function of $(A_{\parallel} + 2A_{\perp})/3$. It can be seen that, in both cases, the orientation of the mesogenic groups becomes smaller as the nematic film thickness is increased. However, this effect is much more pronounced for PA6 than for PA2; the orientation of PA6 decreases rapidly with increasing the thickness, while the orientation of PA2 changes only slowly. For most film thicknesses, the orientation of PA6 is smaller than that of PA2. However, for very thin films, the orientation of PA6 is greater, with a P_2 of ~0.7, which is similar to that obtained as a result of the magnetic field effects (see *Figure 4*).

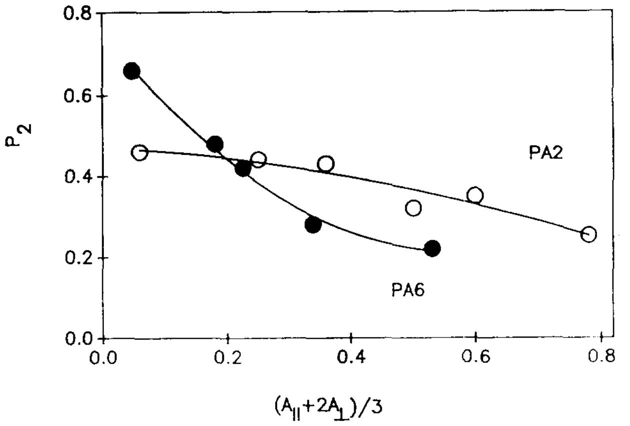


Figure 5 Order parameter as a function of $(A_{\parallel} + 2A_{\perp})/3$ (absorption at 2230 cm^{-1}) for PA2 stretched at 102°C and PA6 stretched at 122°C

This thickness dependence is very significant. The highest orientation for both PA2 and PA6 was achieved for very thin films, with the order parameters corresponding to an almost perfect alignment of the nematic domains. In these drawing experiments, the stress field can only be transferred from the supporting PVA film to the nematic polymer film through their interface. It is conceivable that the alignment of the nematic domains starts in the interfacial region and then could propagate throughout the sample by virtue of a strong cooperative movement among the nematic domains. The propagation is similar to that proposed for a magnetic field-induced orientation in a main-chain LCP[14]. As the infra-red dichroism measures the average orientation, the observed thickness effect can be explained by a weakening of the alignment when the nematic domains are becoming far away from the interface. The difference between PA2 and PA6 results from their different efficiencies in propagation of the alignment. This propagation should be developed through the medium of the surrounding polymer main chains and is more efficient for PA2 because of the stronger coupling interactions between the movements of the mesogenic groups and the chain backbone, and thereby PA2 exhibits a smaller film thickness effect on the orientation.

Finally, we want to mention another utilization of this stretching approach. It enables one to easily prepare oriented LCP samples, and it is convenient to use these samples to study various properties concerning these LCPs in general. For example, the thermal relaxation behaviour of the aligned nematic domains can readily be investigated by placing an oriented sample at a desired ageing temperature for different times before being cooled to room temperature for the polarized infra-red measurements. It was found that for perfectly aligned nematic domains, no relaxation could be observed for almost all temperatures between T_g and T_{cl}, when using ageing times up to 45 min. Relaxation could be caused by thermal energy only at temperatures very close to T_{cl}. Examples of these results are given in *Figure 6*, where the P_2 values of two oriented PA2 samples are plotted

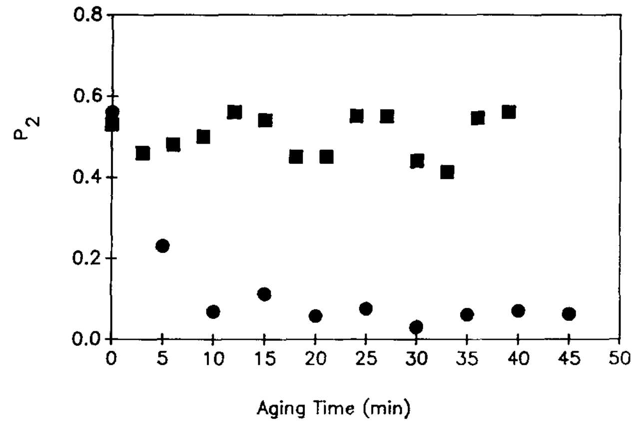


Figure 6 Order parameter as a function of ageing time for oriented PA2 samples held at 104°C for ageing periods of 3 min duration (■) and 5 min duration (●)

as a function of the ageing time. The relaxation temperature was 104°C, which was only 1°C below T_{cl}. One of the samples was held at this temperature for periods of 3 min before each dichroism measurement at room temperature, while the other one was held for a period of 5 min before the measurements were made. In other words, the sample was held at 104°C for an ageing period, followed by an orientation measurement, and was then replaced in the oven for another period of ageing, followed by another orientation measurement, and so on. Therefore, the ageing times indicated in *Figure 6* represent accumulated times. It can be seen that when the sample was annealed for 3 min, followed by cooling, the accumulation of the ageing effect only results in an instability of the aligned nematic domains, with the order parameter oscillating at ~0.5. However, when the duration of the ageing period was 5 min, an instability of the alignment develops, and relaxation occurs. The fall of the order parameter to ~0.05 after two periods of 5 min indicates the loss of the mechanically induced macroscopic orientation of the mesogenic groups. However, it seems that even an accumulation of the 5 min ageing periods cannot lead to a completely isotropic polymer, even up to 45 min, and the residual orientation oscillates with time.

CONCLUSIONS

The purpose of this present study is twofold. First, a simple drawing method is shown to be able to induce a rapid macroscopic orientation of the mesogenic groups in the side-chain LCPs. The method is particularly useful for LCPs which have a short flexible spacer group, since it is much more efficient than the magnetic field effects for obtaining a high orientation. It is believed that the concept of using a supporting film to help the realization of mechanical stretching could prove interesting for side-chain LCPs. PVA is shown to be a good supporting polymer because it has a significant interfacial interaction (good adhesion) with the nematic polymers, which is necessary for transfer of the stress field. Secondly, it is demonstrated that the utilization of the infra-red dichroism technique for studying thin films of the side-chain LCPs is made possible as a result of the drawing method. The infra-red measurements show that the mechanically induced orientation of the mesogenic groups in the nematic polymers investigated in this work is similar to that observed for the cross-linked nematic elastomers and is controlled by the alignment of the nematic domains. Compared with the orientation in a magnetic field, the length of the flexible spacer group has an opposite influence on the alignment; a shorter spacer group, with a stronger coupling between the mesogenic groups and the main chain, favours the interaction of the nematic domains with the mechanical field and thus results in a more efficient alignment.

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