Stress-induced orientation in polymer blends containing a side-chain liquid crystalline polymer

Huanli Lei and Yue Zhao*
Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1
(Received 1 February 1993; revised 7 May 1993)

In this paper, we show that mechanically stretching an immiscible blend made from a nematic side-chain liquid crystalline polymer and a conventional polymer is an efficient way to induce a rapid macroscopic orientation of the mesogenic groups along the stretching direction. The basic condition for this achievement is to perform the mechanical stretching at temperatures between the glass transition temperature and the clearing temperature of the nematic polymer in order to take advantage of the intermolecular co-operativity which is indispensable for a rapid alignment of the nematic domains. The alignment is monitored by determining the orientation of the mesogenic groups using the i.r. dichroism technique. The liquid crystalline polymers investigated are two nematic polyacrylates, and the conventional polymers used are a styrene–butadiene–styrene triblock copolymer, which is a thermoplastic elastomer, and a poly(vinyl chloride).

(Keywords: orientation; blends; liquid crystalline polymer)

INTRODUCTION

There is increasing interest in studying the orientation behaviour in side-chain liquid crystalline polymers (LCPs) because it is involved in all their potential applications. A macroscopic orientation of the mesogenic groups can be induced by magnetic, electric, surface and mechanical effects. The important feature of LCPs that makes them different from low molecular weight liquid crystals resides in the fact that this orientation can be conserved by cooling the polymer below its glass transition temperature (T_g). Mechanical stretching is a convenient way to obtain a macroscopic orientation in side-chain LCPs. Unfortunately, stretching these polymers is often difficult to perform because of the problems involved in preparing samples suitable for stretching. Two mechanical approaches can be found in the literature for orienting side-chain LCPs: the first is fibre-drawing from the isotropic state[1], and the second is to prepare nematic elastomers by introducing chemical crosslinks[2,3], which greatly facilitates the stretching.

However, a well-known technique to induce orientation in polymer crystals[4,5] and LCPs[6] is by surface effects. In a recent study[7], we exploited this approach by mechanically stretching some nematic polyacrylates which were cast onto the surface of a supporting poly(vinyl alcohol) film. The i.r. dichroism measurements revealed a macroscopic orientation of the mesogenic groups at a draw ratio (λ) as small as 1.5. The high orientation can only be obtained when stretching the nematic polymers in their liquid crystalline state, that is, the stretching temperatures are between the T_g and the clearing temperature (T_{cl}, nematic to isotropic transition). This clearly indicates a rapid alignment of the nematic domains by the mechanical field effects.

Very little attention has been paid to the orientation behaviour in polymer blends containing a side-chain LCP. Uzman *et al.*[8] have investigated some blends containing either a liquid crystalline polyacrylate or a liquid crystalline polymethacrylate. Poly(methyl methacrylate) and polycarbonate were the thermoplastic matrices used in their study. The X-ray scattering technique was used to observe the orientation in the LCP which occurred during fibre-drawing from the isotropic melt. They demonstrated the effects of the morphology and the interfacial tension in the blends and showed that an orientation was obtained for the liquid crystalline polyacrylate, but was absent for the liquid crystalline polymethacrylate investigated. No quantitative measurements of the orientation were reported. In the light of our recent study[7], it can be expected that fibre-drawing from the isotropic state would not be an efficient way to produce high orientation of the mesogenic groups in polymer blends because of the absence of mesophases. The objective of the present study is to confirm, once again, the prime necessity of stretching LCPs in their liquid crystalline state in order to obtain high orientation of the mesogenic groups. We investigate the orientation by stretching polymer blends at temperatures between T_g and T_{cl} of the LCP component. I.r. dichroism is used to determine the order parameter of the mesogenic groups. Two nematic liquid crystalline polyacrylates and two conventional polymers, styrene–butadiene–styrene triblock copolymer (SBS) and poly(vinyl chloride) (PVC), are used. As will be shown, stretching the polymer blend containing a side-chain LCP in its liquid crystalline state is very efficient for obtaining high macroscopic orientation of the mesogenic groups along the mechanical field direction.

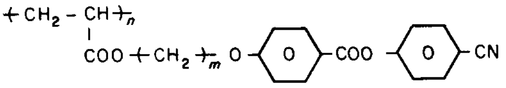
---

* To whom correspondence should be addressed

0032-3861/94/010104-06

EXPERIMENTAL

The liquid crystalline polyacrylates investigated in this study have the following structure:



Two samples, which differ in the length of the flexible spacer, were used: PA2 with $m=2$ and PA6 with $m=6$. They were prepared by a method described in the literature[9]. Both polymers have only a nematic mesophase, exhibiting a nematic to isotropic transition temperature or T_{cl}. The characteristics of the samples are given in *Table 1*. The transition temperatures (T_g and T_{cl}) were determined from a differential scanning calorimeter (Perkin–Elmer DSC-7) using a heating rate of 20°C min^{-1} and a sample weight of ~ 10 mg. The molecular weights were estimated by g.p.c. using polystyrene standards.

The nematic polyacrylates were blended with two conventional polymers: an SBS containing 30% styrene, and a PVC. Both polymers were purchased from Aldrich. The SBS is a well known thermoplastic elastomer. Its high elasticity arises from the presence of the rigid polystyrene (PS) microdomains which are interconnected by the rubbery polybutadiene (PB) chains and support their elastic extension upon stretching. The SBS sample can easily be stretched at temperatures below 65°C which approaches the T_g of the PS microdomains. Therefore, it is useful for blending with PA6 in which the liquid crystalline state starts from temperatures above 33°C. The PVC sample can be stretched at temperatures above its T_g which is ~ 70°C. Therefore, its blends with PA2 and PA6 can be stretched at temperatures corresponding to the liquid crystalline state of the nematic polymers. Thin films of the blends, with a nematic polymer concentration ranging from 5 to 20 wt%, were obtained by casting a 10% tetrahydrofuran solution onto the surface of a glass plate. The solvent was removed by drying the films under vacuum at 60°C for several days. The film thickness was of the order of 40 μm. The immiscibility between the nematic and conventional polymers for all blends studied was obvious from visual observations, namely the films were opaque. As will be shown below, d.s.c. measurements also indicate phase separation in these blends.

The film samples were stretched by using a hand-driven apparatus constructed in our laboratory. The stretching experiments were carried out at well controlled temperatures with a strain rate of ~ 50 mm min^{-1}. Following stretching, the samples were rapidly cooled to room temperature and then used for the orientation measurements. In the case of the highly elastic SBS-containing blends, the stretched samples were kept under tension for the orientation measurements, while for the PVC-containing blends, the extension of the samples was preserved after cooling. Small ink marks were put on the surface of the films before stretching in order to accurately measure λ which is defined as $\lambda = l/l_0$, where l_0 and l are the sample lengths before and after stretching, respectively.

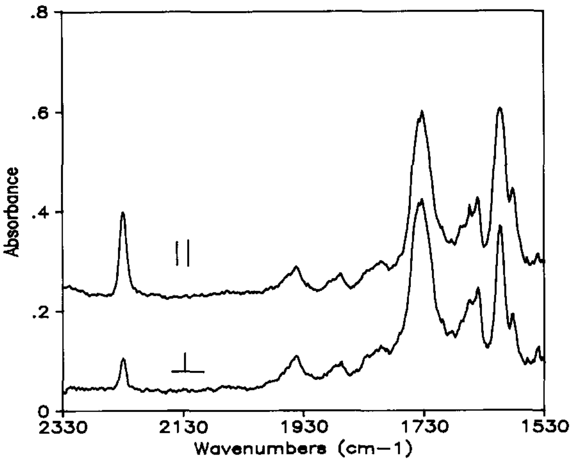


Figure 1 Polarized i.r. spectra of a SBS/PA6 (90/10) blend sample stretched to $\lambda = 2$ with the electric vector parallel (||) and perpendicular (⊥) to the stretching direction

Table 1 Characteristics of the nematic polyacrylates

Sample	T_g (°C)	T_{cl} (°C)	M_n	M_w/M_n
PA2	75	105	34000	1.47
PA6	33	125	56000	2.70

I.r. dichroism measurements on stretched samples were performed on a Bomen-MB102 Fourier transform i.r. spectrometer. The polarized i.r. spectra were recorded from a total of 50 interferograms at a resolution of 4 cm^{-1}, and a wire-grid polarizer was placed between the sample and a DTGS detector to polarize the i.r. beam. The orientation of the mesogenic groups is the alignment of their long axis which is defined as the line connecting the centres of the two phenylene rings. An example of the i.r. dichroism observed for the stretched samples is given in *Figure 1*, which shows the polarized spectra, in the 1530–2330 cm^{-1} region, for a film of the SBS/PA6 (90/10) blend stretched to $\lambda = 2$. The 2230 cm^{-1} band, which is assigned to the stretching vibration of the C≡N group in the mesogenic group, exhibits a strong dichroism: the absorbance with the i.r. beam polarized parallel to the mechanical stretching direction, $A_{\parallel}$, is much greater than that with the polarization perpendicular to the stretching direction, $A_{\perp}$. This indicates a preferential macroscopic orientation of the mesogenic groups along the mechanical field direction. The orientation was measured by determining the order parameter P_2 which can be calculated from the 2230 cm^{-1} band by[10]:

$$P_2 = (3\langle\cos^2\theta\rangle - 1)/2$$
$$= 1.06(R-1)/(R+2)$$

where θ is the angle between the stretching direction and the long axis of the mesogenic groups, and the i.r. dichroism ratio R is given by $R = A_{\parallel}/A_{\perp}$. P_2 ranges from 0 for a random orientation to 1 for a perfect orientation, and it is a measure of the average orientation over all mesogenic groups.

RESULTS AND DISCUSSION

SBS blends

Two SBS blends containing 10 and 20% PA6 were prepared for investigation of the orientation. Before discussing the results, it should be mentioned that, similar to the behaviour of the pure SBS, the blend samples were highly elastic. Their films could easily be stretched to an extension of several hundred per cent, and the initial length was almost recovered when the extensional forces were removed. The SBS polymer used is known to have a morphology with rigid PS microdomains embedded in a rubbery PB matrix[11]. The d.s.c. measurements on these blends clearly indicate a T_g near 33°C which arises from the phase-separated nematic polymer and another two T_gs at ~66°C and ~ −90°C which are due to the PS microdomains and the PB matrix, respectively. For the sake of clarity, the d.s.c. curves in the 10–150°C region are shown in *Figure 2*. It is interesting to notice the different T_{cl}s in the two blends; the T_{cl} in the blend containing 10% PA6 shifts to 122°C which is ~6°C below that of the blend with 20% PA6, and both differ from that of the pure PA6 (125°C). Therefore, it is likely that, in spite of the obvious immiscibility, some significant interfacial interactions exist between PA6 and SBS, and they are dependent on the amount of nematic polymer in the blend.

The strain–orientation behaviour of the mesogenic groups for the blend containing 10% PA6 is shown in *Figure 3*, where the order parameter P_2 obtained at the stretching temperature of 55°C is plotted as a function of λ. First, it can be seen that the orientation increases rapidly upon stretching. At a small λ (1.5), i.e. only 50% extension, P_2 is ~0.26. For comparison[11], the orientation of the rubbery PB chains in this SBS sample at 50% extension is revealed by a P_2 of ~0.05. At higher extensions ($\lambda > 2$), P_2 increases very slowly and reaches a maximum value of ~0.5. This result indicates a rapid and very strong macroscopic alignment of the directors of the nematic domains along the stretching direction, which gives rise to the macroscopic orientation of the mesogenic groups. At perfect alignment, P_2 should be of the order of 0.7 for PA6, which is the local order parameter within the nematic domains[7].

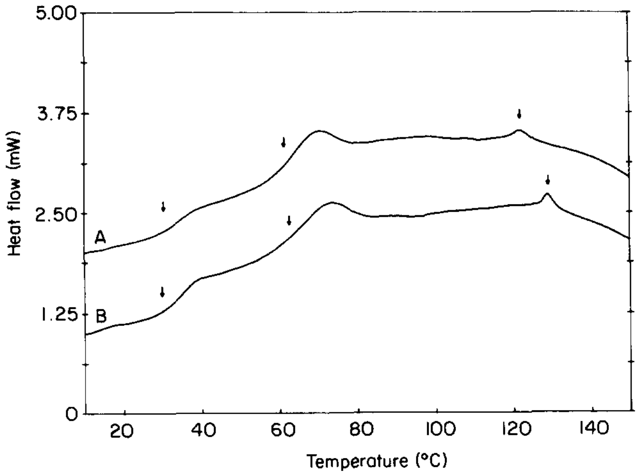


Figure 2 D.s.c. curves of SBS/PA6 blends: (A) 10% PA6; (B) 20% PA6

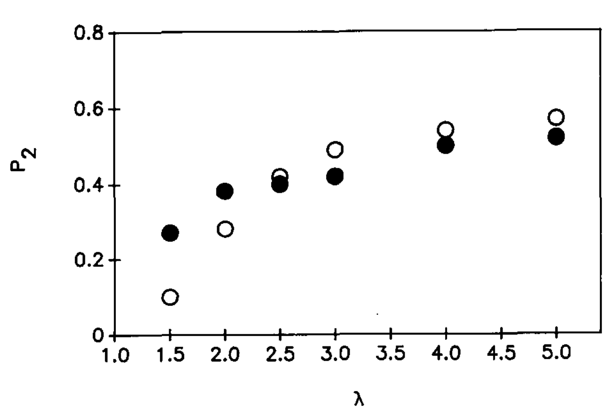


Figure 3 Order parameter *versus* draw ratio for SBS/PA6 blend: (●) stretching at 55°C; (○) relaxation at room temperature after being stretched to $\lambda = 5$ at 45°C

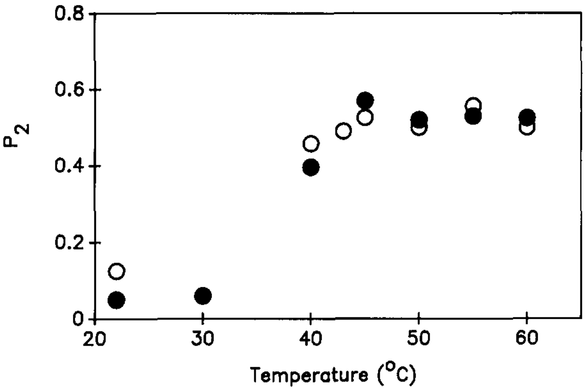


Figure 4 Order parameter *versus* stretching temperature for SBS/PA6 blends: (●) 10% PA6; (○) 20% PA6

Also, in the same figure is presented the relaxation of the aligned nematic domains upon elastic recovery of the sample length. The blend sample used was first stretched to $\lambda = 5$ at 45°C to induce the high orientation, and then the stretched sample was relaxed at room temperature and used for the orientation measurements. It is clear that the relaxation, which can be seen from the decrease in orientation, follows a similar pattern to the orientation development with extension. The relaxation rate is slow up to $\lambda = 2.5$ and then becomes much more rapid for further extension decrease. These results imply that the alignment of the nematic domains in PA6 is related to the elastic extension of the rubbery PB chains.

Figure 4 shows the maximum orientation ($\lambda \geq 3$), for the two blends containing, respectively, 10 and 20% PA6, as a function of the stretching temperature ranging from room temperature to 60°C (the films broke at higher stretching temperatures). As can be expected, at temperatures below the T_g of PA6, the attainable orientation of the mesogenic groups is very small, indicating the absence of a significant alignment of the nematic domains. No necking was observed for these stretchings. For other temperatures between T_g and T_{cl}, the high orientation is almost constant, and there is no difference for the two concentrations of PA6 used in the blends. It is clear that a rapid macroscopic alignment can only be induced by mechanical forces when the LCP is stretched in its liquid crystalline state.

The results presented above show that by stretching an elastic matrix containing a phase-separated nematic polymer, a macroscopic orientation of the mesogenic groups can effectively be obtained. However, this orientation is lost during the elastic recovery of the sample even at temperatures below the T_g of the nematic polymer. Now, it is interesting to know whether or not we can preserve this orientation. In the case of SBS, it is well known[12] that when a stretched sample is annealed under strain, the orientation of the rubbery PB chains, which is responsible for the elastic recovery, can be lost because of the rearrangement of the PS microdomains; consequently, the sample which is initially stretched to

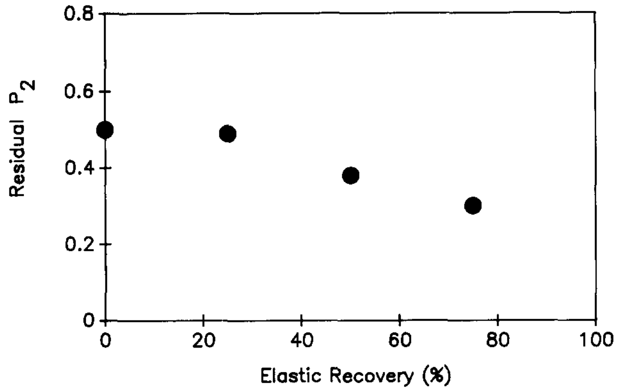


Figure 5 Residual order parameter *versus* elastic recovery of the sample length for SBS/PA6 (90/10) blend

a draw ratio λ_i can no longer recover its length before stretching ($\lambda = 1$), and there is a residual draw ratio λ_r. It was shown[11] that λ_r is directly proportional to the lost orientation of the PB chains. The elastic recovery of the sample length after annealing can be defined as $(\lambda_i - \lambda_r)/(\lambda_i - 1)$. So, it is interesting to investigate the orientation of the mesogenic groups in the annealed samples which exhibit no or little elastic recovery.

For this experiment, the blend samples containing 10% PA6 were first stretched to $\lambda_i = 3$ at 45°C to get the maximum P_2 at ~ 0.5. These samples were then annealed under strain at different temperatures below 65°C for 20 min in order to induce the loss of the orientation of the matrix PB chains. Then at room temperature, after releasing the sample from the stretching device, the residual extension (λ_r) was determined and the orientation of the mesogenic groups in the relaxed sample was measured. The result is shown in *Figure 5*, where the order parameter is plotted as a function of the elastic recovery of the sample length after annealing. It can be seen that there is no loss of the orientation in the samples having no or small elastic recovery, that is, the total macroscopic alignment of the nematic domains can be preserved. Then the orientation decreases with increasing elastic recovery, but it remains high. This result clearly indicates that losing the elastic recovery of the sample is efficient for preserving the macroscopic orientation.

PVC blends

We also used a PVC sample as the matrix for blending with PA2 and PA6. Two concentrations for each of the nematic polymers, 5 and 20%, were used. *Figure 6* shows the d.s.c. curves of the blends containing 20% nematic polymers. In the case of the PA6 blend, two T_gs at ~ 33°C and ~ 70°C indicate the separated phases of PVC and the nematic polymer. One can see that the endothermic peak of the nematic to isotropic transition is broadened and shifts to lower temperatures, suggesting more interfacial interactions between both polymers. As for the PA2 blend, the situation is less clear. The T_g of PA2 is similar to that of PVC, and no T_gs can be distinguished. No clear T_{cl} can be seen; only a very weak transition seems to occur at ~ 90°C. This possibly is caused by more interfacial interactions between PA2 and PVC. As will be seen below, this difference between the PA2 and PA6 blends is reflected by the orientation behaviour in both nematic polymers.

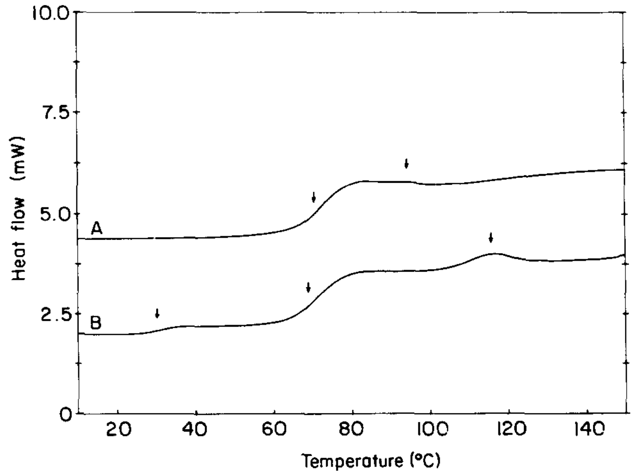


Figure 6 D.s.c. curves of (A) PVC/PA2 and (B) PVC/PA6 blends. The concentration of the nematic polymers was 20%

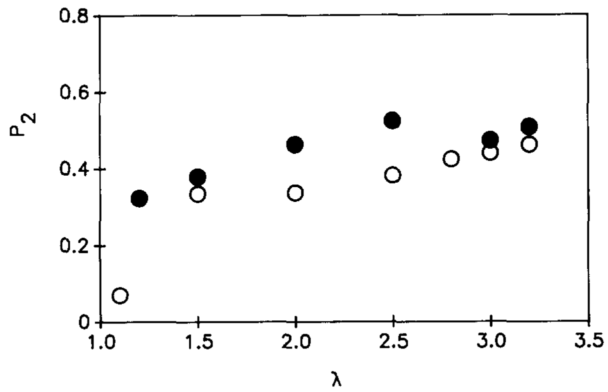


Figure 7 Order parameter *versus* draw ratio for (○) PVC/PA2 and (●) PVC/PA6 blends stretched at 85°C. The concentration of the nematic polymers was 5%

The stretching-induced orientation of the mesogenic groups in the blends containing 5% PA2 and PA6, respectively, is depicted in *Figure 7*. The stretching temperature used, 85°C, is between T_g and T_{cl} of both nematic polymers. It can be seen that, in both blends, the orientation increases drastically upon stretching with a P_2 of >0.3 at $\lambda = 1.5$. On the other hand, it seems that the maximum order parameter, which is ~ 0.4, can be achieved at smaller λ values for PA6 compared to PA2. The results in *Figure 7* again demonstrate the very high efficiency for obtaining a rapid and strong macroscopic alignment of the nematic domains by blend stretching.

The effects of the stretching temperature on the maximum orientation of the mesogenic groups in PA2 and PA6 are shown in *Figures 8* and *9* for the blends containing 5 and 20% nematic polymers, respectively. Several observations can be made. First, the orientation is higher in the blends containing 5% PA2 and PA6 than in the blends with 20%. Then, for both nematic polymer concentrations, the orientation starts to drop at stretching temperatures around the measured T_{cl}s. The sharp orientation decrease for PA2 takes place at much lower temperatures compared to PA6, which simply results from the different T_{cl}s for the two polymers. This is consistent with the conclusion made in our previous study[7], that is, stretching the nematic polymer in its liquid crystalline state is necessary for taking advantage of the intermolecular co-operativity and obtaining a strong macroscopic alignment of the nematic domains. Finally,

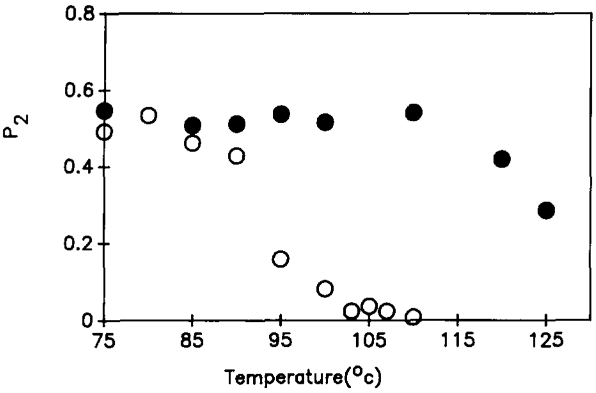


Figure 8 Order parameter *versus* stretching temperature for (○) PVC/PA2 and (●) PVC/PA6 blends. The concentration of the nematic polymers was 5%

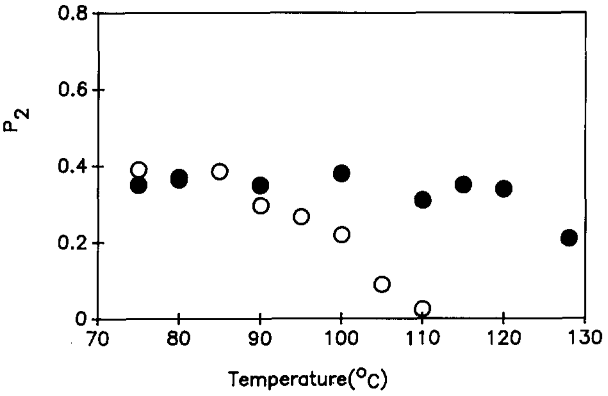


Figure 9 Order parameter *versus* stretching temperature for (○) PVC/PA2 and (●) PVC/PA6 blends. The concentration of the nematic polymers was 20%

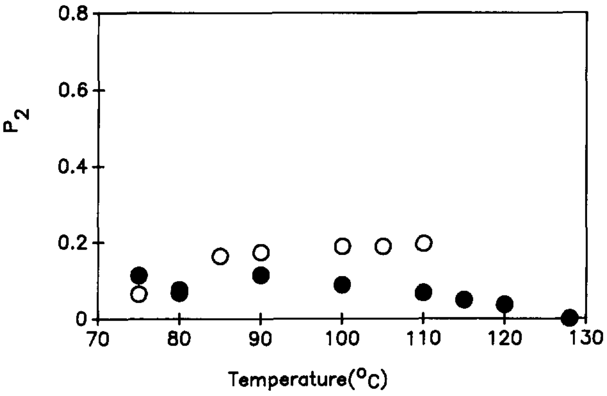


Figure 10 Order parameter of PVC *versus* stretching temperature for (○) PVC/PA2 and (●) PVC/PA6 blends. The concentration of the nematic polymers was 20%

combined with the d.s.c. results (*Figure 6*), it is likely that the nematic state of PA2 in the blends with PVC is markedly weakened, in particular in the blend containing 5% PA2, which results in the drop of the orientation at ~95°C, that is, 10°C below the measured T_{cl} in pure PA2 (*Table 1*).

In these blends containing a side-chain LCP, it should be interesting to be able to observe simultaneously the orientation of the conventional polymer matrix. The orientation of PVC can be determined from the 1423 cm^{-1} band[13] which is not overlapped by any bands of either PA2 or PA6. For the stretched samples used in *Figure 9*, the order parameter of PVC was determined. The results are given in *Figure 10*. It can be seen that the orientation of PVC is much lower than that of the nematic polymers before their drop. This difference is particularly important for PVC in the blend with PA6. The orientation of PVC in the PA6 blend is comparable to the behaviour of pure PVC; higher stretching temperatures lead to lower orientations because of the greater relaxation of the chains which occurred during stretching. The orientation of PVC is higher in the PA2 blend. As mentioned above, this could reflect the difference in the interactions between PVC and PA2, and PVC and PA6. However, the more important feature revealed in these results is that there is no sharp change of the PVC orientation at stretching temperatures where the drop of the orientation of the mesogenic groups in the nematic polymers is observed. For instance, the orientation of PVC in its blend with PA2 remains at the maximum level at 110°C, while the orientation in PA2 drops to zero at this stretching temperature. On the other hand, for the PA6 blend, the orientation of PVC approaches zero at 120°C, while the orientation in PA6 stays at a maximum before the drop. This clearly indicates that the increase in macroscopic alignment of the nematic domains essentially is not related to the orientation level of the matrix polymer chains, but is controlled by the liquid crystalline state. Although the interfacial interactions could be important for transferring the stress field to the nematic polymer, the co-operative effects between the mesogenic groups prevail in the alignment process.

CONCLUSIONS

We demonstrate that mechanically stretching an immiscible blend containing a side-chain nematic LCP can effectively induce a rapid macroscopic alignment of the directors of the nematic domains along the stretching direction, giving rise to high orientation of the mesogenic groups. Such a stress-induced orientation was observed in the blends made from two very different polymer matrices, namely SBS and PVC, emphasizing the primary condition for the alignment of the nematic domains, that is to perform the stretching of the nematic polymers in their liquid crystalline state. However, the interfacial interactions between the phase-separated nematic and conventional polymers could be important for transferring the stress field to the nematic polymer and activating the alignment process.

Furthermore, the investigation on the SBS blends suggests that the elastic extension and recovery of the elastomer matrix chains control the alignment of the nematic domains. This macroscopic alignment can be preserved by annealing the stretched samples under strain, leading to loss of the orientation of the rubbery PB chains which is responsible for the elastic recovery of the sample length. As for the PVC blends, the simultaneous observation of the orientation of the mesogenic groups and that of PVC clearly indicates that the drop of the macroscopic alignment of the nematic domains revealed at higher stretching temperatures is not related to the orientation of the matrix polymer, but is governed by the liquid crystalline state.

ACKNOWLEDGEMENT

The authors thank NSERC (Canada) and FCAR (Québec) for financial support of this study.

REFERENCES

1 Zentel, R. and Strobl, G. R. *Makromol. Chem.* 1984, **185**, 2669
2 Barnes, N. R., Davis, I. J. and Mitchell, G. R. *Mol. Cryst. Liq. Cryst.* 1989, **168**, 13
3 Schätzle, J., Kaufhold, W. and Finkelmann, H. *Makromol. Chem.* 1989, **190**, 3269
4 Wittmann, J. C. and Lotz, B. *Prog. Polym. Sci.* 1990, **15**, 909
5 Bassett, G. A., Blundell, D. J. and Keller, A. *J. Macromol. Sci. Phys.* 1967, **B1**, 161
6 Finkelmann, H. and Rehage, G. *Adv. Polym. Sci.* 1984, **60/61**, 99
7 Zhao, Y. and Lei, H. *Polymer* in press
8 Uzman, M., Kühnpast, K. and Springer, J. *Makromol. Chem.* 1989, **190**, 3185
9 Portugall, M., Ringsdorf, H. and Zentel, R. *Makromol. Chem.* 1982, **183**, 2311
10 Zhao, Y. and Lei, H. *Macromolecules* 1992, **25**, 4043
11 Zhao, Y. *Macromolecules* 1992, **25**, 4705
12 Pakula, T., Saijo, K. and Hashimoto, T. *Macromolecules* 1985, **18**, 2037
13 Chabot, P., Prud'homme, R. E. and Pézolet, M. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 1283