*Macromolecules* **1995,** *28,* 2819–2824

# Side-Chain Liquid Crystalline Ionomers. 2. Orientation in a Magnetic Field

**Philippe Roche and Yue Zhao***

*Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1*

*Received October 7, 1994; Revised Manuscript Received February 1, 1995*[⊗]

ABSTRACT: Orientation behavior in a 5.9-T magnetic field was investigated through infrared dichroism of a nematic side-chain liquid crystalline polyacrylate and two of its ionomers containing around 10 mol % of the units of sodium salt of acrylic acid, prepared through partial alkaline hydrolysis. On the basis of a comparative study, it was found that the magnetic alignment of the nematic domains was severely limited by the presence of the ionic aggregates mainly due to their effect of reducing the polymer chains mobility, which increases the elastic constraints and effectively hinders the orientation of the mesogenic groups. Further, the maximum achievable orientation, which was lowered as the ion content increased, was found to be obtained at temperatures closer to the nematic to isotropic transition temperature. The orientation of the flexible spacer linking the mesogenic groups to the chain backbone was also determined, and on the basis of a large number of data a coupling constant of ca 0.54 was obtained between the orientations of the two constituents for all the samples.

## Introduction

Recently we have shown[1] that side-chain liquid crystalline ionomers could be prepared through partial alkaline hydrolysis of liquid crystalline polyacrylates bearing either a phenyl benzoate or a biphenyl moiety in the side group. The presence of the ionic aggregates has a profound effect on the nematic to isotropic transition temperature, $T_{ni}$, which decreases as the content of the ionic groups increases; but in general, interestingly, the associated transition enthalpy as well as the glass transition temperature are not much affected. The main purpose of that study was to explore a convenient method of making ion-containing and mesophase–displaying polymers which could, eventually, lead to useful materials.

In another line of thought, if we reasonably assume that the nematic order in such ionomers is altered by the ionic aggregates somehow, as could be manifested by the depression of $T_{ni}$, these ionomers provide an interesting system for investigations of the correlation between the intrinsically oriented microstructure and the macroscopic orientation induced by the known external aligning fields (electric, magnetic, mechanical, and surface effects), since other parameters such as the degree of polymerization and the length of the flexible spacer are unchanged. This aspect certainly deserves to be studied because, as is recognized, a suitable control and manipulation of the macroscopic orientation is of crucial importance for commercializing the applications of side-chain liquid crystalline polymers (LCPs).

In this paper, we report a study of orientation behavior of the LC ionomers in a magnetic field. On the basis of the results, the effects of the ionic aggregates on the process of the magnetic alignment will be discussed.

## Experimental Section

**Samples.** The details on the synthesis and characterization of the polyacrylate-based LC ionomers were given elsewhere.[1] For the present study, a LC polyacrylate bearing a biphenyl moiety and two of its ionomers bringing randomly distributed units of sodium salt of acrylic acid were utilized. Their molecular structure and phase transitions (determined by DSC) are summarized in Table 1. The two ionomer samples, namely, P2 and P3, differ in the content of the ionic groups, but have the same $T_g$ which is only 2 °C lower than that of P1, the initial polymer containing no ionic groups; while the $T_{ni}$'s are much lower for the ionomers as compared with P1 (10 and 29 °C lower for P2 and P3, respectively). The initial polymer has a $\bar{M}_n$ of ca. 79 000 g/mol (estimated by GPC, with polystyrene standards), and for the ionomers the degree of polymerization was expected to be unchanged after the partial hydrolysis reaction.

**Magnetic Alignment.** The magnetic orientation of the samples was measured by means of the infrared dichroism, mainly based on the procedure described in a previous paper.[2] As schematically depicted in Figure 1, a thin film of the sample (ca. 30 $\mu$m thick) was prepared by casting a THF solution onto the surface of a KBr window (supporting substance). After the film was dried under vacuum at 60 °C for several days, the whole (film/KBr) was fixed in a 10-mm-diameter NMR tube, and placed in a Bruker WM-250 NMR spectrometer equipped with a temperature controlling unit (±0.5 °C). In this way, a 5.9-T magnetic field could be applied parallel with respect to the film surface for the magnetic orientation. Unless otherwise stated, each sample was first heated to $T_{ni}$ + 12 °C (in the isotropic state) and held at this temperature for 10 min, and then it was cooled, as quickly as possible, to a prefixed temperature between its $T_g$ and $T_{ni}$ for the magnetic alignment. After the desired period of time the sample was removed rapidly from the spectrometer, and quenched at room temperature to freeze the induced macroscopic orientation.

**Orientation Measurements.** The oriented samples were studied by polarized infrared measurements using a Bomen MB-102 FTIR spectrometer (100 interferograms for each spectrum, 4-cm$^{-1}$ resolution, and a wire-grid polarizer placed between the film and the DTGS detector). As expected, the magnetic orientation of the different constituents in the samples could be simultaneously investigated by the infrared dichroism. This is illustrated by the example given in Figure 2, where are shown the two polarized infrared spectra of a P1 film exposed to the magnetic field at 95 °C for 30 min. The high parallel dichroism, i.e., $A_\parallel$ is greater than $A_\perp$ ($A_\parallel$ and $A_\perp$ being the absorbances with the infrared beam polarized parallel and perpendicular, respectively, to the magnetic field direction), for the 2230- (C≡N stretching), 1602-, and 1510-cm$^{-1}$ (phenyl C—C stretching) bands indicates a strong macroscopic orientation of the mesogenic groups along the field direction; in the same direction a significant orientation of the flexible spacer, which contains five $CH_2$ units and links the mesogenic group to the chain backbone, is evident from the

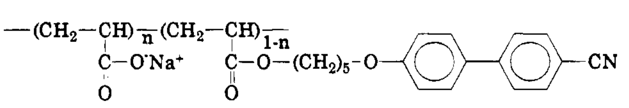
---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1995.

0024-9297/95/2228-2819$09.00/0

**Table 1. Molecular Structure and Phase Transition Temperatures of the Samples**



| sample | $n$ (mole fraction)[a] | phase transitions (°C)[b] |
|---|---|---|
| P1 | 0 | g39 n 117i |
| P2 | 0.07 | g37 n 107i |
| P3 | 0.09 | g37 n 88i |

[a] Expected values based on the amount of NaOH in the hydrolysis reactions. [b] Abbreviations: g, glassy; n, nematic; i, isotropic.

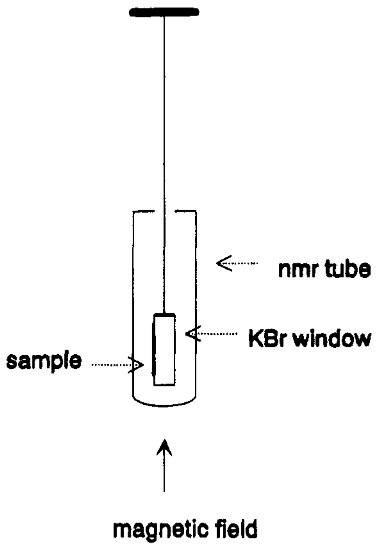


**Figure 1.** Schematic representation of the experimental setup used for the magnetic orientation.

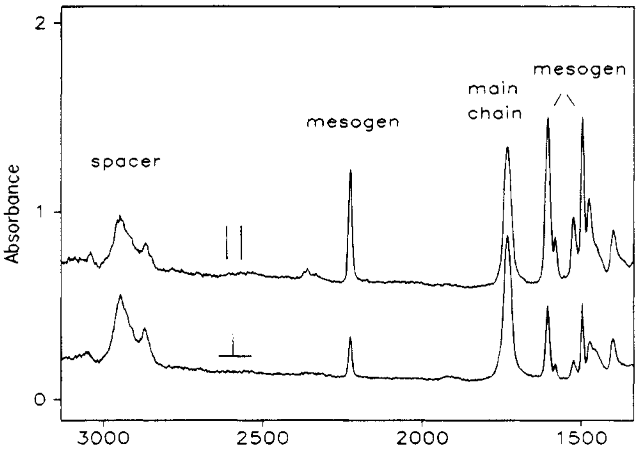


**Figure 2.** Polarized infrared spectra of a P1 films exposed to the magnetic field at 95 °C for 30 min, with the electric vector of the infrared beam parallel (||) and perpendicular (⊥) to the field direction.

perpendicular dichroism of the 2939 cm$^{-1}$ band ($CH_2$ antisymmetric stretching); and, finally, the chain backbone shows negligible orientation judging from the dichroism of the 1735-cm$^{-1}$ band (C=O stretching).

The magnetic orientation was characterized using the order parameter, $P_2$, which is a measure of the average orientation over all the molecular units considered and which is related to the infrared dichroism.[3] In this study $P_2$ of the mesogenic groups was determined by using the C≡N band according to $P_2 = (R - 1)/(R + 2)$, where $R = A_{\parallel}/A_{\perp}$. The calculation of $P_2$ for the flexible spacer with the 2939-cm$^{-1}$ band should take into account the contribution from the $CH_2$ units in the main chain. If the orientation of main chain is known on the basis of the 1735-cm$^{-1}$ band, this can easily be done. Actually, throughout the present study no, or at best only very slight, orientation of the chain backbone was detected within the error of the measurements, and the calculation of $P_2$ for the flexible spacer was simplified to[4] $P_2 = -2.4(R - 1)/(R + 2)$. For each film sample, after the magnetic orientation several measurements of $P_2$ were made, covering the entire surface area and the average value of $P_2$ was calculated and reported. The error bars shown in the figures indicate the standard errors.

## Results

**Orientation of Mesogenic Units.** The magnetic orientation with time, at three temperatures chosen as example, for the initial polymer and the ionomers are shown in Figure 3. Several common features can be seen. First, the orientation is highly temperature dependent. Second, the orientation development basically follows an exponential manner and can be described by $P_2 = [1 - \exp(-t/\tau)]P_{2,\max}$, where $P_{2,\max}$ is the apparent plateau value and $1/\tau$ is a measure of the rate to achieve this value. Third, at certain temperatures a decrease of $P_2$ can be observed at longer orientation times, which is most clear for P1 at 100 °C (Figure 3a). This seems unlikely to be only due to the scattering of data since repeated experiments with those orientation times showed similar results. At this point we do not know if this is a significant phenomenon associated with some kind of instability of the samples in the magnetic field or if it is simply due to the sample preparation or handling (e.g. moisture) which could influence the results. It should be mentioned that the scattering of data is important owing to the inherent experimental difficulties. Each data point reported in Figure 3 represents a separate experiment with, often, a new film sample. Another difficulty involved in applying the magnetic field and counting the orientation time is that a finite length of time was required for cooling the sample from the isotropic state to the prefixed temperature in the NMR spectrometer and, consequently, some magnetic orientation could occur during the cooling and before the sample reached the investigation temperature. This explains the nonzero values of $P_2$ at 0 min in Figure 3.

To reveal the effects of the ionic aggregates on the magnetic orientation an appropriate comparison needs to be established between the polymer and the ionomers. A kinetic analysis of the orientation process, through determination of $\tau$,[5] is of interest but, unfortunately, could not be done with certainty because of the scattering of data. Nevertheless, it is worth while to mention that fitting the curves in Figure 3 yields a $\tau$ whose value ranges from ca. 6 to 10 min, and no meaningful differences could be found between all the samples investigated. The other significant parameter, which can be measured with better precision, is then the apparent plateau $P_2$ value, $P_{2,\max}$, which represents the achievable magnetic orientation at the temperature considered. For each temperature it was calculated by averaging the data obtained at the different times longer than 20 min (except for the case of P1 at 100 °C where only the data before the drop were used). Now the question arises on how to compare $P_{2,\max}$ of the polymer and the ionomers which have similar $T_g$ but different $T_{ni}$ (Table 1), as it is known that the orientation temperature relative to both transitions is important for the magnetic orientation of LCPs.[5,6] Higher temperatures, i.e., more distant from $T_g$, mean greater chain mobility, which favors the orientation of the mesogenic

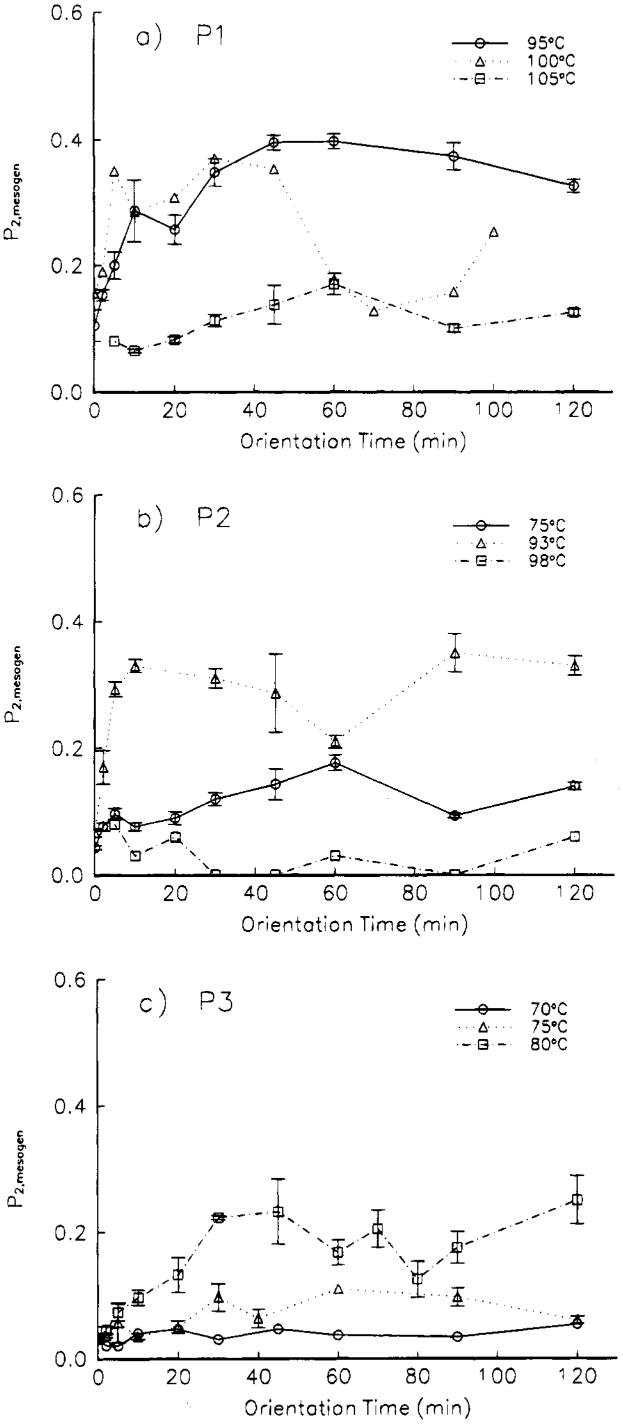


**Figure 3.** Order parameter $P_2$ of the mesogenic groups vs orientation time for the polymer containing no ionic groups (a) and the two ionomers (b and c), at the temperatures indicated in the figure.

groups; but, on the other hand, when the temperature is close enough to $T_{\mathrm{ni}}$ significant thermal fluctuations reduce the nematic order and the resulting macroscopic orientation.

Keeping the above in mind, the orientation comparison is made in two ways, plotting $P_{2,\max}$ vs (1) the orientation temperature normalized to $T_{\mathrm{ni}}$, namely, the reduced temperature, which basically characterizes how close is the temperature to $T_{\mathrm{ni}}$, and (2) the difference between the orientation temperature and $T_g$ normalized to the extent of the temperature range between $T_g$ and $T_{\mathrm{ni}}$, $(T - T_g)/(T_{\mathrm{ni}} - T_g)$, which is a measure of how far the temperature from $T_g$ is relative to the extent of the temperature range of the liquid crystalline state. The results are shown in Figure 4, and the effects of the ionic aggregates are evident from both plots. First, the achievable orientation at most temperatures, except at $T/T_{\mathrm{ni}}$ higher than ca. 0.97, is smaller in the ionomers than in the polymer containing no ionic groups, and the difference is greater for P3, the ionomer carrying more ionic groups. Second, the maximum achievable orientation for the ionomers is not only lowered but also appeared at temperatures closer to $T_{\mathrm{ni}}$, as is revealed by higher $T/T_{\mathrm{ni}}$, and farther from $T_g$ relative to $T_{\mathrm{ni}} - T_g$, i.e., higher $(T - T_g)/(T_{\mathrm{ni}} - T_g)$. Once again, this change is greater as the ionic content increases. For instance, it is seen, from Figure 4a, that the $T/T_{\mathrm{ni}}$ which results in the maximum achievable orientation shifts from ca. 0.94 for the polymer to 0.96 and 0.98 for the ionomers P2 and P3, respectively.

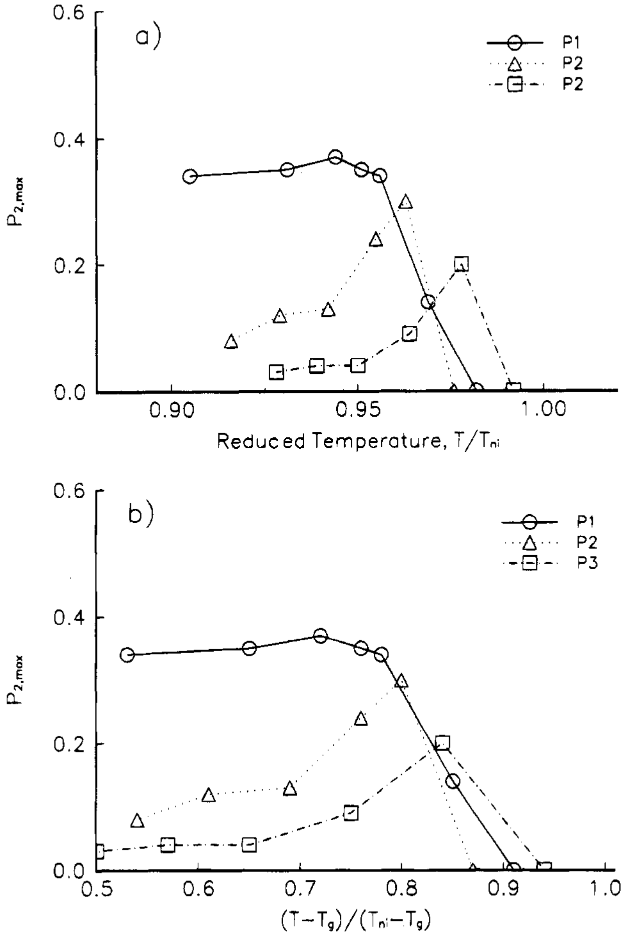


**Figure 4.** Comparison of the achievable orientation between the polymer containing no ionic groups and the two ionomers: (a) order parameter vs reduced temperature, and (b) order parameter vs normalized difference between the orientation temperature and $T_g$.

We also made another series of measurements by using a different procedure: the samples were annealed in the isotropic state outside the spectrometer, then placed in the magnetic field at room temperature, and finally heated to the prefixed temperature for orientation. Here, the samples were in the nematic glassy state before the heating and the orientation at temperatures above $T_g$, and the orientation behavior could be altered as compared with the samples cooled from the isotropic state. The results obtained for the polymer and the ionomers, held in the magnetic field for 30 min, are shown in Figure 5 by plotting $P_2$ as a function of the reduced temperature. Despite of the different orienta-

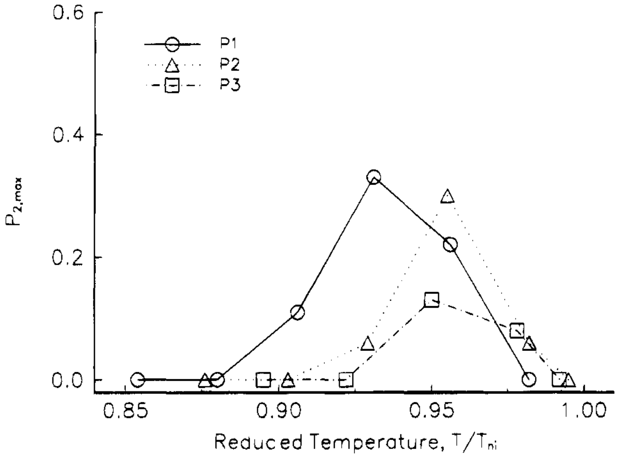


**Figure 5.** Order parameter $P_2$ of the mesogenic groups vs reduced temperature. The samples were heated from room temperature in the NMR spectrometer and held at the orientation temperature for 30 min.

tion conditions the results for most temperature are quite similar to those shown in Figure 4a. The influence of the ionic aggregates is once again revealed by a lower achievable orientation at temperatures closer to $T_{ni}$. But on the other hand, the orientation level at the low investigation temperatures is lowered, particularly for P1. The high orientation of P1 at the lowest temperature in Figure 4a could be contributed by the orientation occurring during the cooling process. It must be emphasized that, for the series of experiments presented in Figure 5, all used samples were freshly prepared, just after drying under vacuum.

**Orientation of Flexible Spacer.** As expected, significant orientation of the flexible spacer was observed. Examples of the plots of $P_2$ vs orientation time are given in Figure 6 for the polymer and the ionomer P3, oriented at the same temperatures as in Figure 3. Basically, the same observations can be made as for the orientation of the mesogenic groups, except that the spacer's orientation is lower. Clearly their orientation in a magnetic field is induced by the alignment of the mesogenic groups owing to the direct linkage. Figure 7 shows a plot of $P_{2,\mathrm{spacer}}$ vs $P_{2,\mathrm{mesogen}}$ for a large number of measurements made on the polymer and the two ionomers. Considering the scattering of data, it is reasonable to assume that a linear relationship exists for all the samples: $P_{2,\mathrm{spacer}} = \kappa P_{2,\mathrm{mesogen}}$, and the regression yields the coupling constant $\kappa = 0.54$.

## Discussion

The purpose of this work is to investigate the effects of the ionic aggregates on the magnetic orientation in the LC ionomers. The use of the initial polymer containing no ionic groups as a reference for comparison should be justified. The two ionomers prepared by partial alkaline hydrolysis contain about 10 mol % of the ionic moieties, which corresponds to a dilution of the mesogenic side groups. It is known that such a dilution could reduce $T_{ni}$, but with 10 mol % or less of nonionic, nonmesogenic comonomeric units the effect is small (often $T_{ni}$ reduced by a few degrees), particularly for the side-chain LCPs having a relatively long flexible spacer.[7] The drastic depression of $T_{ni}$ in the ionomers (29 °C for P3) should mainly be due to the ionic effects. Therefore, it would be reasonable to assume that the differences in the orientation behavior between the ionomers and the initial polymer arise mainly from the effects of the ionic aggregates. However, it would be straighter to use a reference polymer with the same amount of the nonmesogenic side groups as the LC ionomer, but these comonomeric units are nonionic.

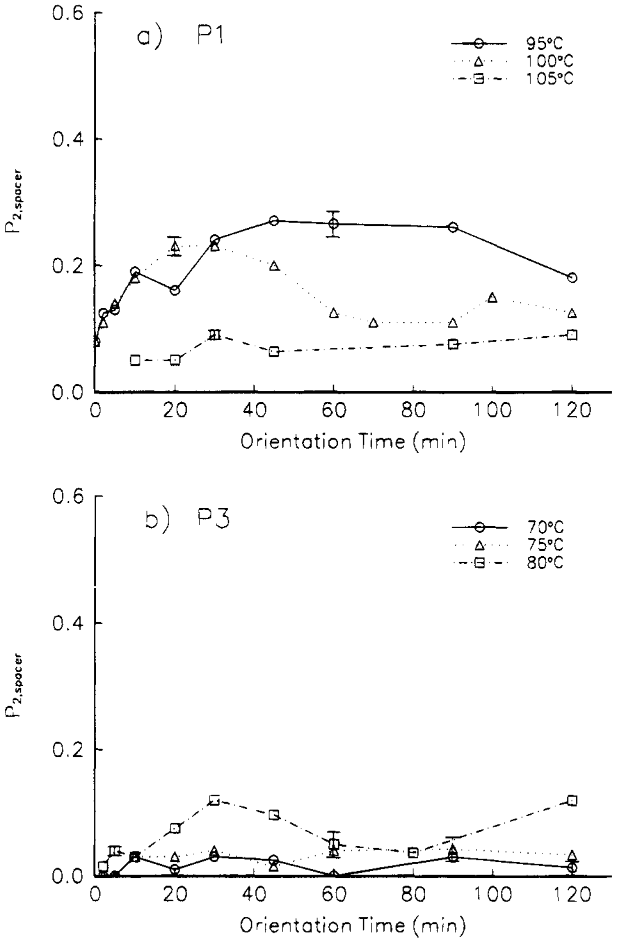


**Figure 6.** Order parameter $P_2$ of the flexible spacer vs orientation time for the polymer containing no ionic groups (a) and one of the ionomers (b), at the temperatures indicated in the figure.

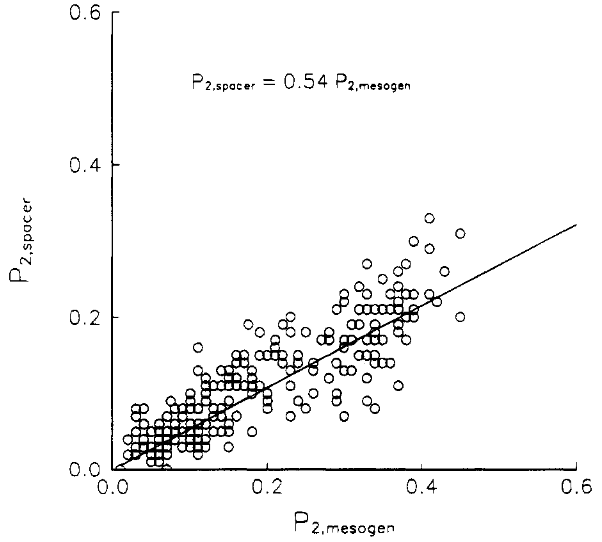


**Figure 7.** Plot of $P_{2,\mathrm{spacer}}$ vs $P_{2,\mathrm{mesogen}}$ for all the samples investigated. Linear regression yields the coupling constant indicated in the figure.

The results reported in this paper show that the perturbation of the microstructure in a liquid crystalline polyacrylate by the presence of the ionic aggregates has severe consequences on the macroscopic orientation of the mesogenic groups in a magnetic field. To discuss the observed decrease of the achievable orientation in the ionomers, it is convenient to express the measured order parameter $P_2$ as $P_2 = P_{2,N}P_{2,D}$, where $P_{2,N}$ characterizes the molecular order within the nematic domains, i.e., the preferred orientation of the mesogenic groups along the director, and $P_{2,D}$ measures the orientation of the nematic domain directors with respect to the magnetic field direction. It is known[5,6] that the magnetic force essentially aligns the nematic domain directors along the field direction and determines $P_{2,D}$. Obviously, a change in the measured $P_2$ can be due to changes in both $P_{2,D}$ and $P_{2,N}$, the latter is related to the intrinsically oriented microstructure in nematic polymers. Two possibilities should be envisaged for interpretation.

The first possibility is that, as the mobility of the polymer chains anchored to the ionic aggregates is reduced,[8] which means fewer available conformations for the chain backbone, the nematic order of the mesogenic side groups could be disturbed, resulting in a lower $P_{2,N}$. If this is the case, a lower $P_2$ is expected even though the ionomers have the same magnetic alignment of the nematic domains as the polymer (same $P_{2,D}$). We have evaluated $P_{2,N}$ on the basis of mechanically inducing the maximum orientation associated with a monodomain structure, through the stretching of thin sample films cast onto the surface of a supporting poly(vinyl alcohol) film,[9] and a similar value of ca. 0.45 was found for the polymer and the ionomers. This suggests that the average nematic order is not significantly affected by the ionic aggregates in these ionomers, and the observed lower magnetic orientation should mainly be due to a lower alignment of the nematic domains, i.e., a smaller $P_{2,D}$, induced by the magnetic effects. This second possibility is more likely.

Indeed, the alignment of the nematic domains necessitates rotation of the mesogenic groups and distortion of the chain backbone which tends to keep a random coil conformation. The ionic groups in the ionomers could, on one hand, promote specific intermolecular interactions involving the mesogenic groups and, thus, increase the effective rotation viscosity $\eta$ which is reversely related to the rate of alignment:[5] $1/\tau \propto \Delta\chi B^2\eta^{-1}$, where $\Delta\chi$ is the anisotropy diamagnetic susceptibility and $B$ is the applied magnetic field. Although an accurate determination of $1/\tau$ was not possible in this study, the possible increase in $\eta$ in the ionomers cannot be ruled out. Actually, the greater alignment for the polymer which occurred during the rapid cooling from the isotropic state to relatively low temperatures ($T/T_{ni} \approx 0.9$), as is revealed in Figure 4, could be an indication of a faster orientation rate as compared with the ionomers. On the other hand, it is clear that the reduced chain mobility in the ionomers could render the distortion of the chain backbone more difficult; this means an increase in the internal elastic constraints for the mesogenic groups and can effectively limit the achievable alignment (orientation) in a magnetic field. Of course all these effects are stronger when the content of the ionic groups is higher.

By inspection of the comparison made in Figure 4, it is interesting to notice that, within errors of the experimental measurements, the apparent maximum values of $P_{2,max}$ for the ionomers, which were achieved at higher reduced temperatures, fall into the line of the initial polymer showing the drop of $P_{2,max}$ with $T/T_{ni}$. This result indicates that, with increasing the ionic content, the ionomer needs to approach more and more $T_{ni}$, where the isotropization process starts, to get great chain mobility and to overcome the ionic effects. It seems that in this region of temperatures the thermal fluctuations, which reduce the nematic order, become the dominant factor on the achievable magnetic alignment, and the macroscopic orientation for the polymer as well as the ionomers is simply determined by the reduced orientation temperature.

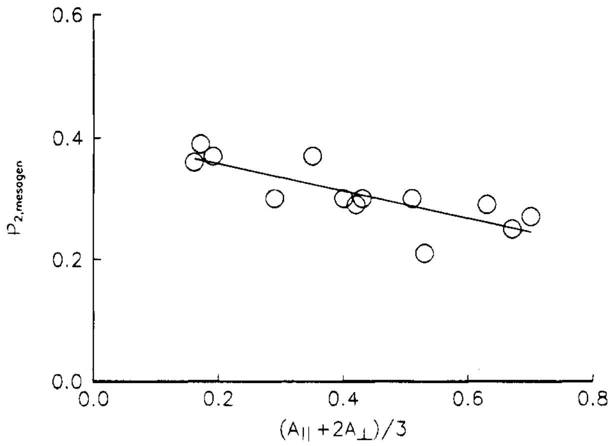


**Figure 8.** Order parameter $P_2$ of the mesogenic groups vs film thickness expressed by $(A_{\parallel} + 2A_{\perp})/3$ (absorption at 2230 cm$^{-1}$) for P1 held at 92 °C for 30 min.

Finally, although all sample films were cast onto untreated surfaces of KBr windows in this study, a possible effect of the window surface on the magnetic alignment was examined. Figure 8 shows the orientation of the mesogenic groups of P1 at 92 °C for 30 min, with $P_2$ plotted as a function of the film thickness expressed in terms of $(A_{\parallel} + 2A_{\perp})/3$ at the 2230 cm$^{-1}$ band (corresponding film thickness ranging from ca. 20 $\mu$m to 60 $\mu$m). It is seen that $P_2$, the average orientation, decreases slightly as the film thickness increases. This, indeed, could be an indication of a greater magnetic alignment of the nematic domains near the window surface, arising from some interfacial interactions which favor the alignment. Whereas, throughout the present work the film thickness was carefully controlled to be similar, this does not affect the conclusions.

## Conclusion

Using side-chain liquid crystalline ionomers, we show that the macroscopic orientation of the mesogenic groups in a 5.9-T magnetic field is greatly affected by the ionic aggregates. The achievable orientation over most temperatures between $T_g$ and $T_{ni}$ was found to be lowered as the ion content increased. Our analysis indicates that a limited alignment of the nematic domain directors should be at the origin, since the nematic order within the domains is similar for the ionomers and the polymer carrying no ionic groups. An increase in the internal elastic constraints, which results from a reduced polymer chain mobility in the ionomers, could effectively hinder the alignment of the nematic domains. Also, it was found that the maximum achievable orientations for the ionomers were obtained at higher reduced temperatures $T/T_{ni}$, in a region where the temperatures are so close to the isotropization process that the thermal fluctuations could become the dominant factor and lead to a lower macroscopic orientation.

**Acknowledgment.** We thank Drs. S. Lacelle, F. Cau, and L. Tremblay (Université de Sherbrooke) for their help in the use of the NMR spectrometer for the magnetic alignment. Financial support from the Natural Sciences and Engineering Research Council of Canada and Fonds pour la Formation de Chercheurs et l'Aide à la Recherche of Québec is also acknowledged.

## References and Notes

(1) Zhao, Y.; Lei, H. *Macromolecules* **1994**, *27*, 4525.

(2) Zhao, Y.; Lei, H. *Macromolecules* **1992**, *25*, 4043.

(3) Jasse, B.; Koenig, J. L. *J. Macromol. Sci. Rev. Macromol. Chem.* **1979**, *C17*, 61.

(4) Looking at the $CH_2$ units in the flexible spacer, the transition moment associated with the 2939 $cm^{-1}$ band is perpendicular to the axis of the alkyl chain, $P_2$ of the spacer can be calculated from

$$P_2 = -2(R' - 1)/(R' + 2) \qquad (1)$$

where $R' = A'_{\parallel}/A'_{\perp}$, $A'_{\parallel}$ and $A_{\perp}$ being the absorbances of the $CH_2$ units in the spacer. While the absorbances which can be measured from the infrared spectra contain the contribution of the $CH_2$ units in the main chain, in other words, the measurable $R$ at the 2939 $cm^{-1}$ band is given by

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

Where $A''_{\parallel}$ and $A''_{\perp}$ are of course the absorbances of the main chain $CH_2$ units. On the basis of a monomeric unit, there are five $CH_2$ units in the spacer and one unit in the chain backbone, we can write

$$(A'_{\parallel} + 2A'_{\perp})/3 = 5(A''_{\parallel} + 2A''_{\perp})/3 \qquad (3)$$

If the main chain orientation is absent

$$A''_{\parallel} = A''_{\perp} \qquad (4)$$

From eqs 2–4 we obtain

$$R' = (17R - 2)/(16 - R) \qquad (5)$$

Substituting $R'$ in eq 1 by eq 5 yields

$$P_2 = -2.4(R - 1)/(R + 2) \qquad (6)$$

(5) (a) Moore, J. S.; Stupp, S. I. *Macromolecules* **1987**, *20*, 282. (b) Anwer, A.; Windle, A. H. *Polymer* **1991**, *32*, 103.

(6) (a) Achard, M. F.; Sigaud, G.; Hardouin, C. W.; Finkelmann, H. *Mol. Crystl. Liq. Cryst. Lett.* **1983**, *20*, 975. (b) Moore, R. C.; Denn, M. M. *High Modulus Polymers, Approaches to Design and Development*; Zachariades, A. E., Porter, R. S., Eds.; Marcel Dekker: New York, 1988.

(7) Barnes, N. R.; Davis, F. J.; Mitchell, G. R. *Mol. Cryst. Liq. Cryst.* **1989**, *168*, 13.

(8) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.

(9) Zhao, Y.; Lei, H. *Polymer* **1994**, *35*, 1419.

MA946032M