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Communications to the Editor

Magnetic Field-Induced Orientation in Side-Chain Liquid Crystalline Polymer Studied by Infrared Dichroism

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One of the prominent features of thermotropic liquid crystalline polymers is that molecular orientation can be generated by magnetic or electric field effects and then be preserved by cooling the polymer below its glass transition temperature (T_g). A number of techniques have been utilized for studying such orientational phenomena; they include nuclear magnetic resonance,[1] X-ray diffraction,[2] electron spin resonance,[3] dielectric relaxation spectroscopy,[4] optical transmittance,[5] and magnetic susceptibility measurements.[6] However, few systematic studies have so far been effectuated on the orientational process in a magnetic field of the side-chain liquid crystalline polymers in which the mesogenic molecule is attached to the polymer backbone as the side group via a flexible spacer. This is partly due to the availability as well as the capability of the used techniques. So it is of interest to develop more efficient experimental methods for the field orientation studies.

In this paper we present our study on the magnetic orientation of a nematic side-chain liquid crystalline polymer by means of infrared dichroism. This technique allows us to determine the average orientation over all mesogenic groups with respect to the magnetic field direction through the measurement of the order parameter P_2 which is defined as

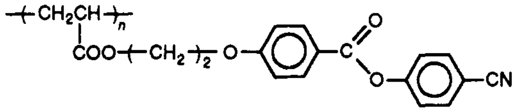
$$P_2 = (3\langle\cos^2\theta\rangle - 1)/2$$

in which θ is the angle between the long axis of the mesogenic molecule and the field direction. Here, it should be emphasized that this average macroscopic orientation is governed by the alignment of the nematic domains in which the mesogenic molecules are preferentially oriented along a director. Obviously, at perfect alignment of these domains, the orientation revealed by infrared dichroism is that of the local orientation in the ordered domains. The order parameter is determined through infrared dichroism measurements according to

$$P_2 = (R_0 + 2)(R - 1)/(R_0 - 1)(R + 2)$$

in which R is the infrared dichroic ratio and given by $R = A_\parallel/A_\perp$, where $A_\parallel$ and $A_\perp$ are the measured absorbances with the infrared beam polarized parallel and perpendicular, respectively, to the field direction, and $R_0 = 2\cot^2\alpha$, α being the angle between the axis of the mesogenic molecule and the transition moment of the infrared vibration used for the orientation measurements.

The nematic polymer investigated is a polyacrylate having the following structure:



The C≡N stretching band at 2230 cm^{-1} is well suited to the orientation measurement for the mesogenic groups, and by defining the molecular axis as the line connecting the centers of the two phenyl rings, the angle α is about 11°.[1b] It follows that P_2 can be calculated from

$$P_2 = 1.06(R - 1)/(R + 2)$$

The polymer has been synthesized by the method described in the literature.[7] Its phase behavior has been measured using a differential scanning calorimeter (Perkin-Elmer DSC-4), showing a T_g at 73 °C and a clearing temperature T_{cl} (nematic to isotropic transition) around 102 °C.

It is believed that the main difficulty for using infrared dichroism to observe the magnetic orientation is to prepare appropriate nematic polymer films which can readily be exposed to the magnetic field with the film surface parallel to the field direction. This is necessary for polarized infrared measurements. In our study, we used a hydrolyzed poly(vinyl alcohol) (PVA) supporting film which is thermally stable up to 220 °C (melting point). Thin nematic polymer films were cast from a 10% chloroform solution onto the PVA film surface and then dried under vacuum at 50 °C for several days. The chloroform is a nonsolvent for PVA, and, more importantly, there is no PVA infrared absorption in the vicinity of 2230 cm^{-1}, enabling the use of the C≡N stretching band to measure the orientation of the mesogenic groups.

Magnetic orientation was induced by placing such films in a 5.9-T magnetic field (Bruker WM-250 NMR spectrometer), equipped with a heating and temperature controlling unit (stability ±0.5 °C). For each measurement, the sample was first heated to 125 °C and retained at this temperature for 15 min, ensuring an isotropic state; then it was quenched to the temperature of orientation (between T_g and T_{cl}) for a desired time before being cooled rapidly to room temperature under the field effects. Polarized infrared measurements were carried out at room temperature on a BOMEN MB-102 Fourier transform infrared (FTIR) spectrometer at a resolution of 4 cm^{-1} and from a total of 50 interferograms for each spectrum. Polarization of the infrared beam was obtained by a wire-grid polarizer placed between the film and the DTGS detector.

Figure 1 shows the polarized infrared spectra, in the 1650–2300-cm^{-1} region, of a film held at 92 °C for 15 min in the magnetic field. A strong infrared dichroism of the 2230-cm^{-1} band is observed, with a much higher absorbance for the electric vector of the infrared beam parallel to the field direction. This clearly indicates an alignment of the nematic domains along the magnetic field.

The dependence on temperature of the magnetic orientation is shown in Figure 2, where the order parameter is plotted as a function of temperature for the same orientation time of 30 min. It can be seen that the magnetic alignment for this nematic polymer takes place over the

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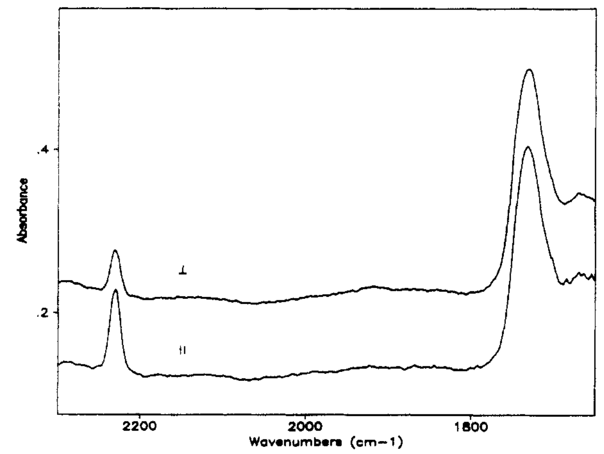

Figure 1. Polarized infrared spectra, in the 1650–2300-cm^{-1} region, of a nematic polymer film exposed to the magnetic field at 92 °C for 15 min, with the electric vector of the infrared beam parallel (∥) and perpendicular (⊥) to the field direction.

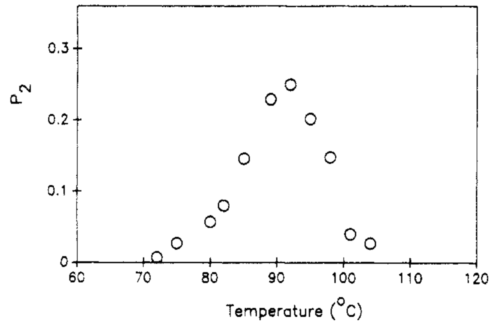

Figure 2. Order parameter vs orientation temperature for nematic polymer films placed in the magnetic field for 30 min.

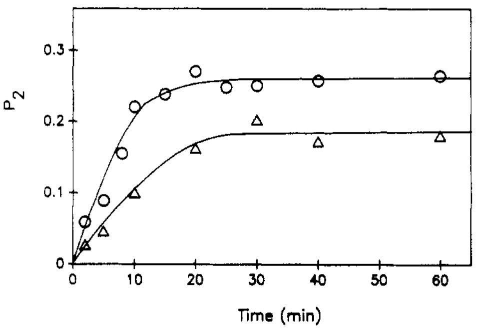

Figure 3. Order parameter vs orientation time for nematic polymer films placed in the magnetic field at 92 (○) and 95 °C (△).

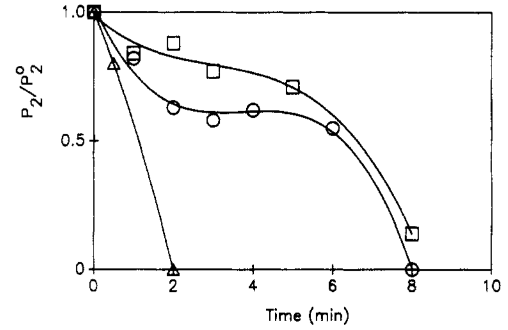

Figure 4. Normalized order parameter vs relaxation time for nematic polymer films in the absence of the magnetic field at 92 (□), 94 (○), and 97 °C (△).

entire temperature range between T_g and T_{cl}, but the orientation level is strongly affected by the temperature. An apparent maximum orientation is observed near 90 °C, i.e., about 20 °C above T_g and 10 °C below T_{cl}. This seems to reflect the influence of the mobility of the polymer main chain and the thermal fluctuation of the nematic phases. The increased orientation with temperature above T_g could be dominated by the effects of an increasing chain mobility (decreasing viscosity) that favors the alignment of the nematic domains, while the reducing orientation at high temperatures closer to T_{cl} could be caused by thermal fluctuations which affect the local orientation in the ordered domains.[2b]

Of particular interest is the convenience to study the magnetic orientation and relaxation kinetics using infrared dichroism. The same sample could be put in the field for different orientation times before quenching, and the initial isotropic state for each measurement was ensured by keeping the sample at a temperature well above T_{cl} for a long enough time. Figure 3 shows the orientation development with time at two temperatures. The orientation increases rapidly at beginning of the process and then reaches a maximum value $P_{2,\max}$ at longer times. Similar to the behavior observed for main-chain nematic polymers,[2d] the time dependence of the orientational process can fairly be described by

$$P_2/P_{2,\max} = 1 - \exp(-t/\tau)$$

where τ is a characteristic orientation time. Fitting the experimental data given in Figure 3 yields $P_{2,\max} = 0.255$ and $\tau = 8$ min for $T = 92$ °C and $P_{2,\max} = 0.18$ and $\tau = 11$ min for $T = 95$ °C.

Another interesting feature revealed in Figure 3 is the influence of the length of the flexible spacer on the magnetic orientation of the mesogenic groups. The nematic polymer investigated in this study has a short spacer (2 methylene units), and its maximum orientation attainable in the field is given by an order parameter P_2 of about 0.26. This orientation is much smaller than that found for the polymers containing a longer flexible spacer (e.g., 6 methylene units), in which P_2 is around 0.5.[1a,3] It has been shown[3,8] that the local orientation in the nematic domains is essentially independent of the spacer length, so it seems likely that in our study only a limited alignment of the ordered domains occurs. This is caused by stronger interactions or couplings between the mesogenic groups and the polymer main chain, hindering the formation of a complete alignment of the nematic domains.

The orientation relaxation of the mesogenic groups in the absence of the field was investigated using the samples oriented in the field at 92 °C, with a resulting P_2 near 0.24. They were placed into a thermostat oven for desired relaxation times and then cooled at room temperature for infrared measurements. Figure 4 shows the rate of orientation relaxation at three temperatures. The order parameters P_2 measured at different relaxation times are normalized to the order parameter before the relaxation process, $P_2°$. It is clear that thermal effects cause relaxation of the aligned nematic regions when the field is removed, and this relaxation is strongly temperature-dependent. Complete relaxation is achieved after about 8 min when the sample is annealed at 94 °C, while at 97 °C the process is over within 2 min. Most interesting is the relaxation behavior manifested at 92 and 94 °C. The loss of orientation is fast in the first 2 min and then slowed down over a period of times, forming an apparent plateau. This is followed by a drop of orientation, completing the relaxation process. This result clearly suggests different steps for thermal relaxation of the nematic domains, which are associated with different time scales. At this stage of work, we have no further explanation for this observed behavior.

To summarize, using a PVA supporting film, the infrared dichroism technique has been demonstrated to be useful for studying thin films of side-chain liquid crystalline polymers in a magnetic field. In particular, it is well suited to studies of the kinetics of magnetic orientation and relaxation. More studies are in progress in our laboratory, and the results will be published later.

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