

Optical Biaxiality of Nematic LC-Side Chain Polymers with Laterally Attached Mesogenic Groups

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Summary

Liquid crystalline polymers with mesogenic groups laterally attached to the polymer backbone were investigated by polarizing microscopy with respect to their optical properties. The nematic polymers were macroscopically oriented in a magnetic or electric field. Polarization microscopic investigations with convergent polarized light show optical biaxial behavior of the nematic phase.

Introduction

The existence of a biaxial nematic phase for thermotropic liquid crystals was theoretically predicted in 1970 by M. J. Freiser (1). The first-order transformation from the isotropic state to an uniaxial nematic state is followed at lower temperature by a second-order transformation to a biaxial nematic state. At this phase transformation the rotation of the molecules around their long molecular axes becomes hindered and the mesogens achieve planar alignment (Fig. 1).

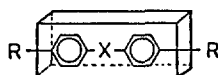


Fig. 1:
Planar structure of mesogenic groups

In the biaxial nematic state, orientational correlations between the molecules exist not only between their long axes but also between their short axes (2). This second order phase transformation has never been experimentally observed for conventional low molar mass liquid crystals (l.l.c.'s) and liquid crystalline side chain polymers because crystallization, the onset of a smectic phase or a transition to the glassy state intervenes at lower temperatures. The existence of a biaxial nematic phase of a liquid crystalline main chain polymer is discussed by M. Kleman (2) and C. Viney et al. (3) but no clear evidence is given for the biaxial phase structure.

Recently we succeeded in preparing a new class of nematic liquid crystalline side chain polymers with mesogenic groups laterally attached to the polymer backbone (4) (Fig. 2).

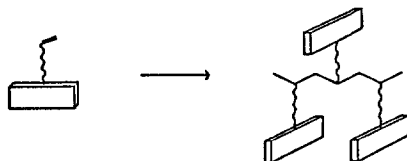


Fig. 2:
Liquid crystalline side chain polymers with mesogenic groups laterally attached to the polymer backbone

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In these systems the long axis rotational motions of the mesogenic moieties are restricted. To determine the optical properties of this new class of nematic polymers, especially with respect to uniaxial or biaxial nematic phase behavior, polarizing microscopic investigations were performed.

Polarizing microscopic observations

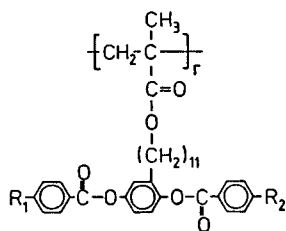
To answer the question if this new class of liquid crystalline polymers exhibit an uniaxial or a biaxial nematic phase, macroscopic homeotropic alignment has to be obtained in order to perform conoscopic investigations. In this macroscopic phase orientation, the long molecular axes of the mesogenic moieties are perpendicular to the surface of the glass slides. Homeotropic orientation of conventional liquid crystalline material can be achieved by two different methods⁽⁵⁾ which can also be applied for the orientation of polymers. Liquid crystalline polymers with a positive anisotropy of magnetic susceptibility ($\Delta\chi$) can be aligned in a magnetic field (Fig. 3), while mesogenic polymers with a positive dielectric anisotropy ($\Delta\epsilon$) can be oriented homeotropically in an electric field (Fig. 3).



Fig. 3: Macroscopic homeotropic alignment of mesogenic groups in an electric or magnetic field

For the homeotropic alignment in an external field, different polymers (1, 2, 3) were used. The phase transition temperatures of these nematic polymers are listed in Table 1.

Table 1: Phase transition of polymers 1, 2, 3, (in K) (g=glassy, n=nematic, i=isotropic)



Polymer	R ₁	R ₂	T _{g,n}	T _{n,i}
<u>1</u>	OCH ₃	OCH ₃	312	337
<u>2</u>	OC ₆ H ₁₃	OC ₆ H ₁₃	282	335
<u>3</u>	OC ₄ H ₉	CN	309	350

Polymers 1 and 2 were oriented in a magnetic field due to their positive $\Delta\chi$. Electric field orientation was used with polymer 3 because of its positive $\Delta\epsilon$, which is a result of the CN-terminal group.

For the orientation of polymers 1 and 2 in the magnetic field, the polymer was introduced between two glass slides. The sample thickness was adjusted to 50 μm by glass spacers. The sample was exposed to a strong magnetic field (7 Tesla) which was applied perpendicular to the glass slides to achieve homeotropic orientation of the mesogens. It should be noted that a weaker magnetic field (1.4 Tesla) did not produce homeotropic orientation. In the magnetic field the sample was kept near the clearing temperature for one hour and then cooled to room temperature.

For the orientation in the electric field polymer 3 was squeezed between glass slides which had conductive coating and 50 μm glass spacers. An ac voltage of 100 V and

50Hz was applied at 77°C and a slow orientation process was observed, accompanied by a change in the birefringence. The sample was annealed overnight in the electric field and then cooled to room temperature.

Conoscopic observations of the oriented polymers 1, 2 and 3 show an interference figure typical for optical biaxial systems (Fig. 4). In the parallel position a split cross of zero birefringence is observed (Fig. 4a). After a 45° rotation of the microscope stage, the interference pattern of the 45° position appears which is characterized by the maximum splitting of the two isogyres (Fig. 4b). A further rotation of 45° yields again a split cross but with the line of zero birefringence turned 90° from the original position. After a 180° rotation from the original position, the original interference figure is obtained. The optical axial angle $2V$ is found to be about 10° for all samples.

The orientation of the molecules with respect to their short axes is not homogeneous throughout the sample. When the glass slides are moved on the fixed microscope stage, the sample gives interference figures which vary between those described above.

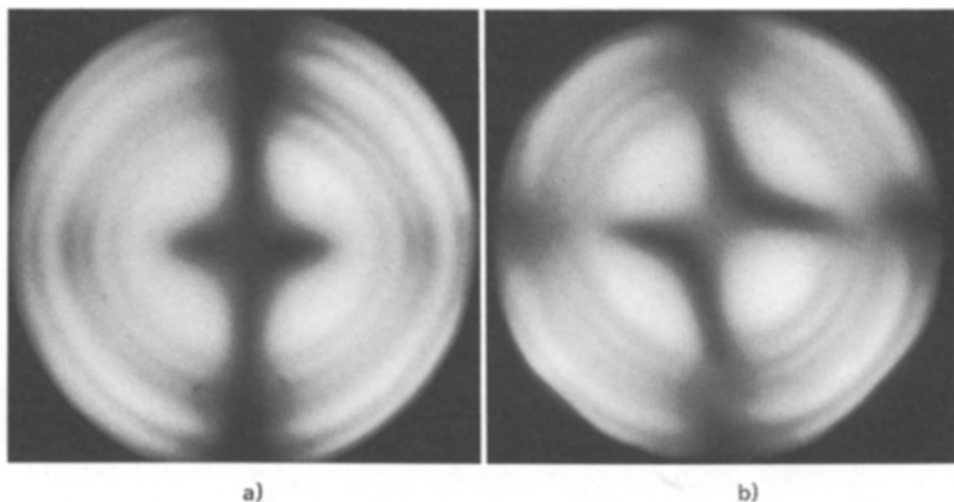


Fig. 4: Conoscopic interference figures of the polymers with the mesogenic groups laterally attached to the polymer backbone with optical biaxial properties
a) parallel position, b) 45° position

Orthoscopic observation exhibit an equilibrium texture which differs from the texture of conventional nematic I.L.c's (6) and of nematic side chain polymers in which the mesogenic groups are attached to the polymer main chain via a terminal spacer (7). Annealing the sample below the clearing temperature overnight gives a texture with different coloured domains separated by inversion walls. Annealing an uncovered thin sample near the clearing temperature for 24 h yields a schlieren texture. For our samples, only ± 1 inclinations can be observed. According to M. Kleman (2), ± 1 inclinations are expected for biaxial nematic phases owing to different elastic constants of these phases.

Conclusion

The optical investigations of macroscopically oriented polymers with mesogenic groups laterally attached to the polymer backbone show optical biaxial nematic phase behavior. These systems confirm that a hindered rotation around the long axes of the mesogenic moieties changes the uniaxial nematic phase structure to a biaxial nematic phase structure. This hindered long axis rotation is achieved by having the mesogenic groups connected laterally to the polymer backbone. To our knowledge these are the first well-defined thermotropic liquid crystalline systems with biaxial nematic phase behavior. This new class of biaxial nematic polymers opens interesting aspects for theoretical considerations and experimental investigations.

Acknowledgements

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