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Morphological properties and birefringences of uniaxial lyotropic nematic mesophases under influence of various magnetic field values

Aykut Evren Yavuz, Özgür Masalcı, Nadide Kazancı*

Department of Physics, Faculty of Science, Ege University at Izmir, Turkey

*Corresponding author. Tel: (+90) 2323881092; Fax: (+90) 2323112833; E-mail: nadide.kazanci@gmail.com

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ABSTRACT

One has studied time-dependent changes of morphological properties of uniaxial lyotropic nematic-calamitic N_C and nematic-discotic N_D mesophases with various external magnetic field values. Also, changes of optical birefringence values of N_C and N_D lyotropic mesophases under influence of the magnetic fields has been investigated based on time. Differences of morphological properties and changing birefringence values between N_C and N_D mesophases have been interpreted according to magnetic field values. The values of optical birefringence and morphological properties changing in time between N_C and N_D mesophases which are opposite signs of diamagnetic anisotropy have been compared with increasing magnetic field values.

Keywords: Lyotropic nematic mesophases; polarizing microscopy; birefringence; magnetic field.

Introduction

Lyotropic nematics, generally formed by solution of amphiphile materials, water and cosurfactants, are anisotropic mesophases of matter and very sensitive to external magnetic fields [**1-3**]. These mesophases are sorted into three types: optically uniaxial nematic-calamitic (N_C) and nematic-discotic (N_D) mesophases and optically biaxial (N_{bx}) mesophase. These mesophases exhibit both a long-range orientational order and a short-range translational one based on formation of miceller aggregates [**4**]. NMR experiments [**5, 6**] investigated that N_C and N_D mesophases have rod-like and disk-like miceller shapes, respectively **[7]**. Differences between the structural properties of the micelles cause N_C and N_D mesophases to have negative optical (Δn<0) and positive optical (Δn>0) anisotropies, respectively [**8**].

One of typical morphological characteristics of nematic mesophases is their spontaneous orientation in magnetic field due to their lower viscosities [**5**]. The morphological properties of the mesophases could thus change when magnetic field has been applied. Two unixial nematic mesophases are also defined by positive and negative diamagnetic anisotropies. N_C mesophase has a positive diamagnetic anisotropy ($\Delta\chi$>0) as director of the mesophase aligns parallel to the magnetic field orientation, which is called planar orientation. On the other hand, N_D mesophase has a negative diamagnetic anisotropy ($\Delta\chi < 0$) since director of N_D aligns perpendicularly to magnetic field orientation, named homeotropic orientation [**9,10**].

The fact that N_C and N_D mesophases exhibit high sensitivity to external magnetic field and also have opposite signs of diamagnetic anisotropy requires these mesophases to be studied under influence of magnetic field. Research on changes in morphological and optical properties of the mesophases dependent on time under influence of magnetic field has hardly seen [**11,12**]. In future, lyotropic nematic liquid crystals could find a wide range of applications because they are sensitive to external physical effects and exist biologically [**13**].

The present study has investigated the texture characteristics and birefringence measurements of oriented samples of N_C and N_D mesophases under influences of different static magnetic field values. Polarizing microscope method has determined textural features to find time-dependent changes of the morphological properties of the mesophases in magnetic fields. Optical birefringence of lyotropic nematics have been measured according to time while applying external magnetic fields.

Experimental

Materials

Lyotropic nematic calamitic (N_C) and nematic discotic (N_D) mesophases have been formed by tetradecyl trimethyl ammonium bromide (TTAB) + water + 1-octanol ternary system. TTAB purchased from Sigma (Cat. No. T-4762) is of high purity (over 99%). Ultra-pure water has been used as solvent and 1-octanol with purity over 99% used as cosurfactant from Merck AG (Cat. No. 100991). Necessary amounts of three components each in the system have been weighed with a precision of 10^{-4} g (And Hr-120) and the mixture stored in hermetically closed vessels. The lyotropic system was kept in thermostat (MEMMERT-UE 400) at a temperature of 308 ± 0.1 K to be homogenized for ten days. The system has periodically been agitated with a vortex shaker (Nüve NM 110). Whether the obtained lyotropic systems are homogeneous has been examined by observing their textures under a polarizing microscope. N_C mesophase has been formed by a sample composition with 32 wt. % TTAB + 67 wt % water + 1 wt. % 1-octanol concentrations and N_D mesophase obtained from another sample composition of 34 wt. % TTAB+ 60 wt. % water + 6 wt. % 1-octanol concentrations.

Measurements

Polarizing microscope method has been employed to define morphological properties of N_C and N_D mesophases. The equipment is Olympus BX-P polarized microscope, Olympus SC35 microphotographic system, special stage, differential thermocouples, special heater-thermostat, λ-plates and interference filters. The thickness of the lyotropic nematic mesophases placed into the sandwich cells was 120 µm. N_C and N_D samples have been placed in static magnetic fields whose values are 0,4 T, 0,6 T and 1 T and which have been applied perpendicularly to the reference surfaces of the sandwich cells. Time-dependent changes of the optical birefringence of the samples under influence of magnetic fields have been determined by compensation method using Berek compensator. All the measurements have been performed at a constant temperature of 298 K.

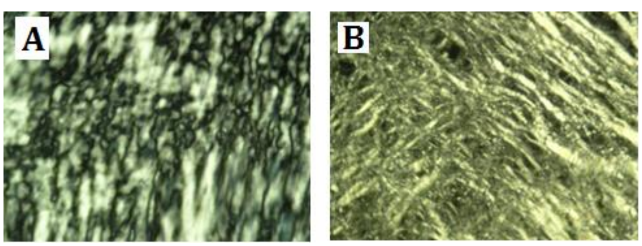

Fig. 1. Lyotropic nematic textures of TTAB/H_2O/1-Octanol lyotropic system, A) nematic-calamitic N_C and B) nematic-diskotic N_D textures, magnification of x100.

Results and discussion

The present study has examined morphological properties of lyotropic uniaxial nematic mesophases excited in various magnetic fields using polarizing microscopy method. In addition, compensation method has studied time-dependent changes in values of their birefringences under the influence of the magnetic fields.

Study of textural morphological properties informs on molecular orientations and is therefore accepted as a standard method to determine mesophases of liquid crystals [**14, 15**]. Polarizing microscopy method has studied morphological properties of N_C and N_D mesophases to establish their similarities and dissimilarities. N_C and N_D mesophases have exhibited typical schlieren textures as in [**16, 17**]. Textures of both mesophases were stable and could be made reproducible. Their textures had threadlike forms, singular points and small uniform regions (**Fig. 1**). On the other hand, spinning microscopy table on which to put the samples enables dark regions to illuminate in N_C and illuminated ones to darken in N_D textures successively, which is related to the fact that optical anisotropic signs of both mesophases are opposite [**14,18**]. The small uniform regions have been observed to be larger in N_C than in N_D. On the other hand, the threadlike formations are denser and longer in N_D than those in N_C. Moreover, the threadlike formations have been seen to turn into flament-like ones. Texture properties similar to those above were also observed in [**16, 19, 20**]. Optical birefringence values for N_C and N_D mesophases have been found to be $1,448.10^{-3}$ and $1,872.10^{-3}$, respectively and are consistent with those in the literature [**17**]. Magnetic fields of 0,4 T, 0,6 T and 1 T have separately been applied to each of N_C and N_D samples and properties of magnetomorphological texture studied in them.

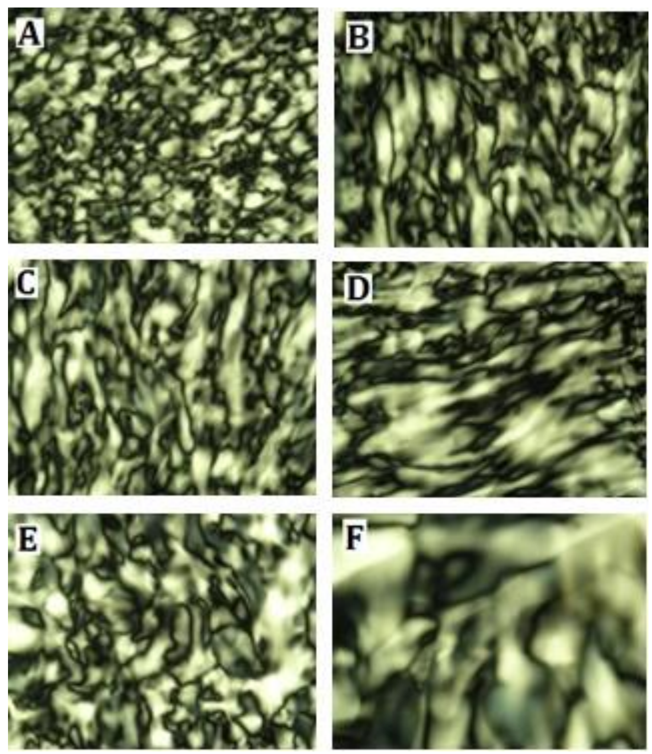

Fig. 2. Texture samples while applying 0,4 T magnetic field after A) 3 and B) 6 hours; while applying 0,6 T magnetic field after C) 3 and D) 10 hours and while applying 1 T magnetic field after E) 3 and F) 11 hours to N_C mesophase. Magnification x100.

Homogeneous magnetic fields of 0,4 T, 0,6 T and 1 T have been applied to samples of N_C and their textural properties exposed to variations (**Fig. 2**). The threadlike formations have disappeared due to influence of magnetic field on the mesophase and planar regions appeared instead. In addition, schlieren formations have been found to lengthen and decrease in density in time. Study of N_C textures of planar orientation under influence of the different magnetic field values has shown the higher value of magnetic field the larger planar regions in time. Clear variations of textural properties have hardly been observed for magnetic fields of 0,4 T, 0,6 T and 1 T after 6th, 10th and 11th hours, respectively.

Magnetomorphological properties have been influenced by homogeneous magnetic fields of 0,4 T, 0,6 T and 1 T in N_D as well as in N_C mesophases. Textures of N_D mesophase applied by the magnetic fields have been observed to change in time. These textures under influence of the magnetic fields have moved to planar orientation from homeotropic orientation and dark pseudo-isotropic regions occured in them (**Fig. 3**). The dark regions in the textures have enlarged more with higher magnetic field value in time. Changes of textural properties have hardly seen after 19th, 22nd and 24th hours for 0,4, 0,6 T and 1 T, respectively. Moreover, the study has shown that inside of some pseudo-isotropic regions has been covered with schlieren formations which also occured in [**21,22**].

Optical conoscopic examinations can determine homoetropic orientation based on conoscopic cross emerging in polarizing microscope [**20**]. In order to find homoetropic orientation of N_D mesophase under magnetic field conoscopic studies have been done. The study has shown that conoscopic cross emerges clearly after 30 minutes under influence of 0,4 T magnetic field and disappears completely after 60 minutes, with the result that homoetropic orientation of the texture has changed to planar orientation under influence of the magnetic field (**Fig. 4**) [**17**].

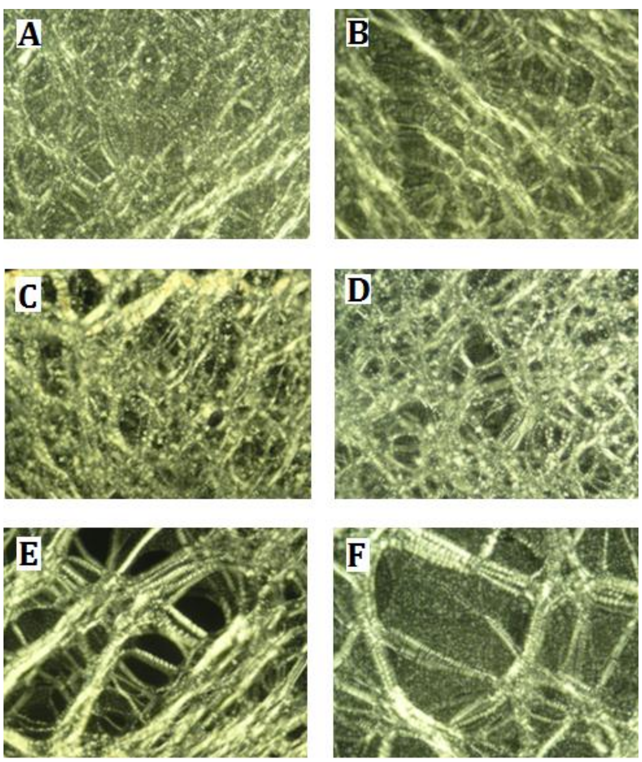

Fig. 3. Texture samples while applying 0,4 T magnetic field after A) 3 and B) 19 hours ; while applying 0,6 T magnetic field after C) 3 and D) 19 hours and while applying 1 T magnetic field E) 3 and F) 15 hours to N_D mesophase. Magnification x100.

Changes in morphological properties of anisotropic mesophase are related to those in its optical birefringence values under influence of magnetic field since changes in morphology of the mesophase depend on orientation of the mesophase director. Thus, the fact that the director orients in magnetic field has an impact on the birefringence values of the mesophase [**23**]. Accordingly, morphological changes in N_D mesophase due to applying the magnetic fields resulted in optical birefringence values changing. Time-dependent changes in birefringence values of the mesophase influenced by three different magnetic field values are shown (**Fig. 5**).

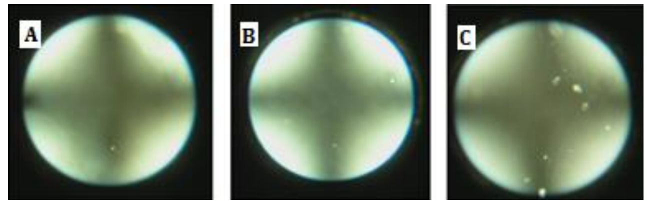

Fig 4. Appearance of conoscopic cross after A) 20 B) 30 and C) 45 minutes.

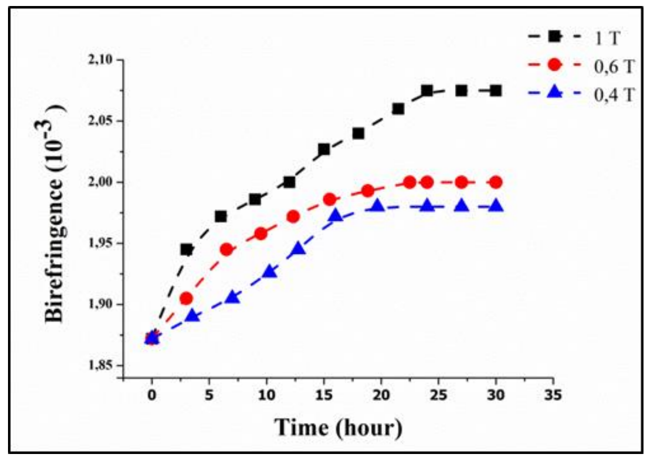

Fig. 5. Optical birefringence values of time-dependent variation of N_D mesophase with $\Delta n>0$ under the influence of magnetic field with 1 T, 0,6 T and 0,4 T.

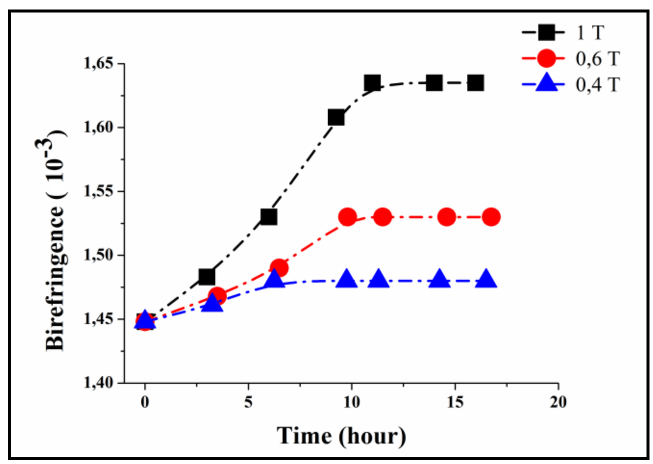

Fig. 6. Optical birefringence values of time-dependent variation of N_C mesophase with $\Delta n<0$ under the influence of magnetic field with 1 T, 0,6 T and 0,4 T.

Changes of birefringence values in N_D mesophase depend on values of the applied magnetic fields, which is theoretically suggested by Palanga et al [**24**]. The texture of N_D sample remained under the influence of 1 T magnetic field for three hours has expanded pseudo-isotropic regions farther than do those influenced by magnetic fields of 0,4 T and 0,6 T. Examination of the textures in saturation under the influence of 1 T has shown that significantly larger pseudo-isotropic regions have formed than others, which is consistent with to the fact that their birefiringence is of greater value . Also, time-dependent birefringence values of N_C mesophase under three different magnetic field values have been found (**Fig. 6**).

The higher value of magnetic field applied in N_C mesophase, the more time-dependent variations in birefringence values just as in N_D mesophase. Planar regions influenced by 1 T magnetic field in N_C mesophase have emerged in larger space than those by 0,4 T and 0,6 T magnetic fields with higher value of birefringence. On the other hand, increasing of magnetic field value has caused longer time in saturation.

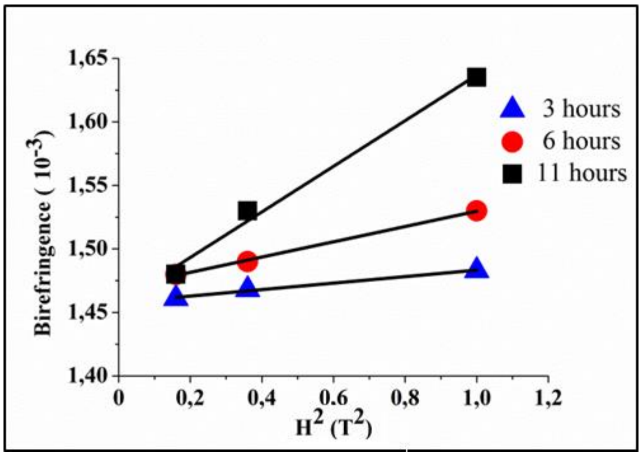

Fig. 7. Graphic Δ*n* = f (H^2) of N_D mesophase in the magnetic fields at 3rd, 9th and 15th hours.

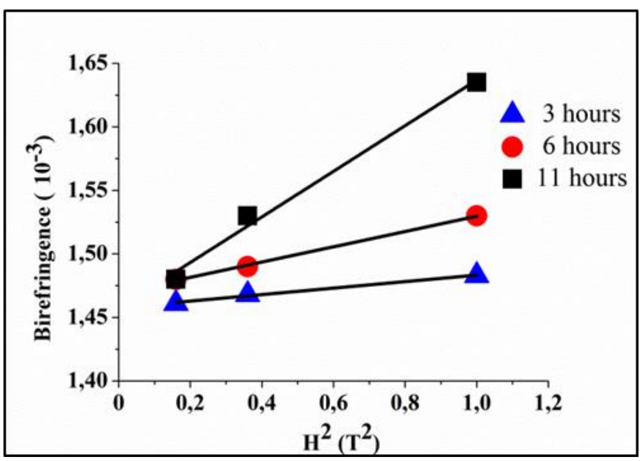

Fig. 8. Graphic Δ*n* = f (H^2) of N_C mesophase in the magnetic fields at 3rd, 6th and 11th hours.

It is concluded that time-dependent changes in birefringence values of N_C mesophase are closely related to those in its morphological properties as in N_D mesophase. Comparison of birefringence values of N_C and N_D mesophases shows N_D has greater absolute value than N_C does, which is confirmed the studies by [**8, 12, 25**]. Birefringence values of N_D and N_C mesophases under influence of magnetic fields applied during the same period of time has changed linearly with the square of the magnetic fields. Illustration of graphics of Δ*n* = f (H^2) to study dependence of birefringence values of lyotropic mesophases on the applied magnetic fields has been shown for both N_D (**Fig. 7**) and N_C mesophases (**Fig. 8**). Furthermore, birefringence values of nematic phase in thermotropic liquid crytals are known to change linearly with square of magnetic fields under certain circumstances [**26, 27**].

Conclusion

Typical schlieren textures of lyotropic nematic-calamitic N_C and nematic-discotic N_D mesophases have been obtained. Textural changes have occurred under the influence of the magnetic field on them. The increased value of magnetic field has accerelated changes in textural morphological properties of N_C and N_D mesophases over time. These changes have achieved saturation after a given time. The studies [**11, 28**] observed that saturation was achieved due to the effect of magnetic field on textures over time as well. The increased value of magnetic field has led to more changes in morphological properties in time and a period of saturation has been achieved later than in lower value of magnetic field. On the other hand, time-dependent changes in values of optical birefringences have been observed and higher value of magnetic field causes those of birefringences in both mesophases to increase. N_C mesophase has achieved saturation faster than N_D mesophase. Because diamagnetic anisotropy is negative, N_D mesophase shows more morphological changes than does N_C, thereby more changes of birefringences occuring in N_D mesophase. The study has found birefringence and morphological changes to be proportional to each other. Indeed, morphological changes influenced values of birefringences in other studies [**23, 29**].

Acknowledgements

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