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The Dielectric Properties of Nematic Liquid Crystal, 5CB Confined to Treated and Untreated Anopore Membranes

Stanisław A. Różański [a], Friedrich Kremer [b], Herbert Groothues [b] & Ralf Stannarius [b]

[a] Maria Skłodowska-Curie High School, W. Pola 11, 64-920, Piła, Poland

[b] Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstr. 5, D-04103, Leipzig, Germany

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THE DIELECTRIC PROPERTIES OF NEMATIC LIQUID CRYSTAL 5CB CONFINED TO TREATED AND UNTREATED ANOPORE MEMBRANES

STANISŁAW A.RÓŻAŃSKI
Maria Skłodowska-Curie High School, W.Pola 11, 64-920 Piła, Poland

FRIEDRICH KREMER, HERBERT GROOTHUES AND RALF STANNARIUS
Fakultät für Physik und Geowissenschaften, Universität Leipzig
Linnéstr. 5, D- 04103 Leipzig, Germany

Abstract In recent years a substantial amount of research has been devoted understanding of anchoring and ordering mechanisms of liquid crystal molecules near solid surfaces. The interaction of a liquid crystalline compound with a solid surface depends on the nature of both the surface and liquid crystal material. The dielectric measurements in untreated Anopore membranes confirm the planar axial order of nematic molecules; in membranes treated by decanoic acid, a polar-radial or polar-polar orientationof the molecules is very likely, although a slight escaped director structure at least at low temperatures seems to be indicated in the dielectric data.

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INTRODUCTION

Surface effects have been studied in nematic liquid crystals (NLC) because they are usually used in display cell where surface properties play a major role in their operation.[1] There are various alignment techniques involving different treatments of the solid surface such as chemical etching, coating with lecithin, adsorption of organic surfactant additives, undirectional rubbing, or the oblique evaporation method.[2] The distance ξ on which the LC-surface interaction is observed has an order of about 10^3 Å.[3] Surface effects may also be probed by confining liquid crystal to porous material. The behavior of NLC in pores the diameter of which is lower then ξ gives information about the nature of LC-surface interactions.

From NMR [4], it is known that the 5CB nematic director in the untreated membranes is aligned parallel to the pores axis (axial case); after lecithin treatment, it is constrained in a radial type of alignment at the surface. Crawford et al. [5] examined the role of surface coupling agents on the aligning and ordering mechanisms at a liquid-crystal solid interface with deuterium nuclear magnetic resonance. The cylindrical channels of Anopore membranes are chemically modified using an aliphatic acid ($C_nH_{2n+1}COOH$) as a surface coupling agent and are filled with the liquid crystal. The planar polar configuration with homeotropic anchoring condition is stable for agents with $n \geq 7$ while chain lengths $n \leq 6$ support a uniform axial configuration with planar anchoring at the cavity wall.

Dielectric studies of NLC have proved to be a valuable source of information on the mesomorphic liquid crystalline phase. It has been shown that the confinement of nematic liquid crystal (NLC) to inorganic filters with regular pores provides a convenient tool for the orientation of the sample in dielectric experiments.[6] The dielectric properties of liquid crystals in porous materials are only briefly explored. By employing broadband dielectric spectroscopy the frequency and temperature dependence of the complex dielectric function is measured. This enables the underlying mechanisms of liquid crystal-solid interface interaction to be investigated and the influence of the anchoring condition on this process to be studied.

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EXPERIMENTAL

The cylindrical channels of Anopore membranes having a diameter 0.2 μm, 0.1 μm and 0.02 μm with porosity 50 %, 40 %, and 35 %, filled with the liquid crystal compound 4-n-pentyl-4'-cyanobiphenyl (5CB), were used to probe molecular interactions occurring near solid surface. The Anopore membrane is composed of an alumina oxide film with cylindrical pores penetrating through its 60 μm thickness perpendicularly to the membrane surface. The high surface-to-volume ratio of these membranes make it useful for dielectric spectroscopy to observe directly surface-induced order. 5CB is a compound of relatively high dielectric anisotropy in the aligned state and makes them particularly suitable for dielectric studies. Additionally the membranes are treated with a 2 wt % solution of decanoic acid ($C_9H_{19}COOH$) in methanol. The membranes are dipped into the solution for about one minute and then quickly pressed between filters in order to remove the solvent from the outer membrane surface, and placed in a vacuum oven for 1 hour to evaporate methanol. The acid head group binds chemically to the surface and the aliphatic chains form a compact array perpendicular to the cavity wall.

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The liquid crystal is introduced into the membranes in the isotropic phase and heated for several hours to ensure a complete filling.

The dielectric study was accompanied by an optical observation of the polarizing light transmission through the membranes. Due to the optical birefringence of the liquid crystal material the optical appearance of the Anopore membrane will depend on the configuration of the liquid crystal within the cavities. Two different types of cylindrical channels were used: those with untreated inorganic wall, and those with aliphatic acid coated channels' surfaces. In absence of aliphatic acid a Maltese black cross characteristic of uniaxial crystal cut perpendicularly to its optic axis is observed. For the planar anchoring conditions the liquid crystal and the alumina membrane are nearly index matched, resulting in a translucent appearance of the membrane. Contrary, in the cylindrical channels of Anopore membranes chemically modified using an aliphatic acid, the strong scattering of the light is observed. The aliphatic acid coated channels induce a homeotropic orientation of the director at the wall, leading to three basic types of nematic director field configuration, i.e. the planar-radial, planar-polar and escaped radial configurations.[5] For a homeotropic configuration the light experiences an effective index of refraction which is mismatched with that of the alumina matrix, resulting in an opaque appearance of the membrane.

RESULTS AND DISCUSSION

For a study of the orientational order of the director field we measured dielectric spectra of the 5CB bulk and adsorbed in treated and untreated Anopore membranes. In the isotropic phase one relaxation process is observed, when in the nematic phase two relaxation processes occurs: first connected with hindered rotation of the molecules around their short molecular axis (flipping process), and second connected with tumbling of the molecules around their short axis. The dielectric strength of the first process is comparable, in the order of magnitude, to the static dielectric anisotropy of 5CB. However, the dielectric strength of the second process is one order of magnitude lower then first one.

In the confined mesophase, the nematic director is aligned perfectly parallel to the pore walls of the filters (axial configuration). The fast process is suppressed in the dielectric spectra of the axially confined NLC sample. In this configuration, only the process connected with flips of the molecules around their short axis is effective (Figure 1). However, in Anopore membranes chemically modified using decanoic acid, the slow process is remarkably suppressed. This gives strong evidence that the nematic director inside the treated filters is oriented nearly perpendicular to the axes of the channels (planar - polar or planar - radial configuration).

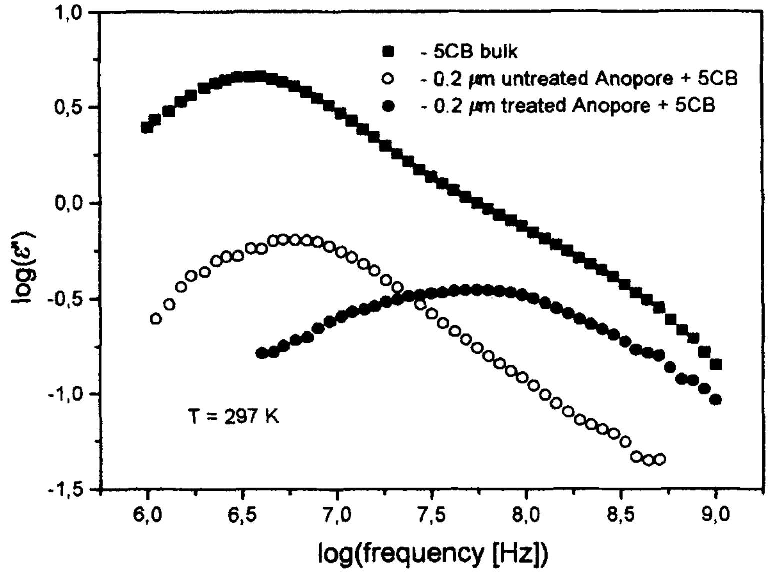

FIGURE 1 Frequency dependence of the dielectric loss ε" for 5CB in the bulk (solid square) and confined to untreated (open circle), and treated (solid circle) Anopore membranes.

Figure 2 shows comparisons between the temperature dependence of relaxation times τ_{max} for the bulk 5CB and confined to treated and untreated Anopore membranes. The temperature dependence of the mean relaxation time τ_{max} exhibits an Arrhenius-like behavior in both isotropic and nematic phases. In the isotropic phase the relaxation rate is nearly uninfluenced by the presence of the inner surfaces and increases with

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decreasing temperature up to phase transition (T_{IN} = 308 K). The activation energy calculated from experimental data is about 36.7 kJ/mol. In nematic phase situation is more complicated. The relaxation time is faster for the porous materials as compared to the bulk, but influence of different diameter of the pores is not very large. The activation energy is about 64.6 kJ/mol and is comparable with data from another experiments.[7]

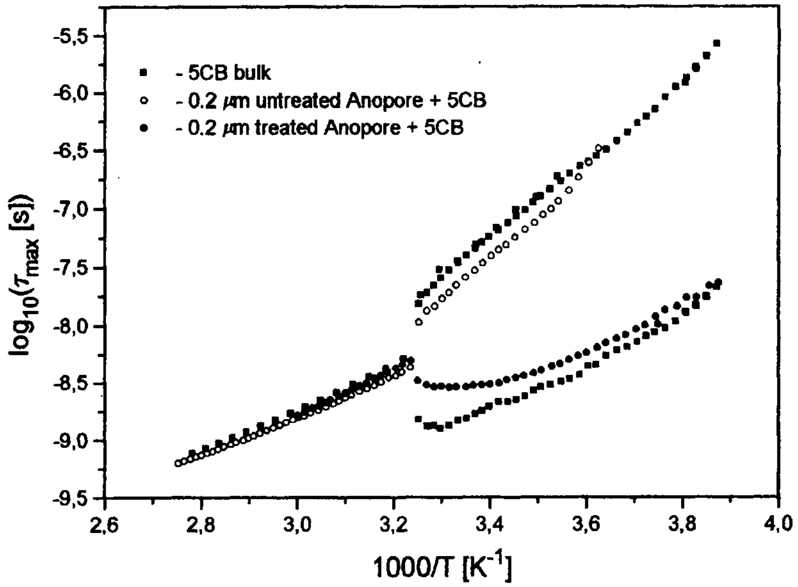

FIGURE 2 Arrhenius plot of the temperature dependence of the relaxation time τ_{max} for the bulk 5CB and confined to untreated and treated Anopore membranes.

However, relaxation rate is about two orders of magnitude faster for the nematic liquid crystal confined to the Anopore membranes chemically modified by aliphatic acid. This dramatic change of relaxation time is connected with reorientation of the molecules from parallel to the channels to perpendicular to the walls of the channels (from planar axial to planar radial). In this situation second process connected with tumbling of the molecules around their short molecular axis is observed. The activation energy far below phase transition yields a value of about 46.3 kJ/mol.

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CONCLUSIONS

The dielectric properties of nematic liquid crystal 5CB confined to treated and untreated Anopore membranes have been measured in the frequency range from 10^6 Hz to 10^9 Hz and at temperatures between 270 K and 320 K. It has been shown that the confinement of NLC to inorganic filters with regular pores provides a convenient tool for the orientation of the sample in dielectric experiments. In the 5CB/Anopore system, with untreated channels walls, only first relaxation process is observed. However, in treated Anopore membranes second process is detectable. The relaxation rate in the isotropic phase is nearly uninfluenced by the presence of the inner surfaces, then in Anopore membranes separation of the two processes is possible. The dielectric strength of the observed processes is considerably weakened for the 5CB/Anopore system. From observed dispersion curve of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ we find, that the anisotropy $\Delta\varepsilon$ of 5CB change sign twice. The dielectric measurements in untreated Anopore membranes confirm the planar axial order of nematic molecules, then in treated membranes by decanoic acid, the polar radial or polar planar orientation of the molecules is observed.

REFERENCES

1. B.Jerome, Rep.Prog.Physics, 54, 391 (1991).
2. P.Sheng, Phys.Rev.Letters, 37, 1059 (1976).
3. L.M.Blinov, E.I.Kac and A.A.Sonin, Uspiekhi Fiz. Nauk, 152, 449 (1987).
4. G.P.Crawford, R.Stannarius and J.W.Doane, Phys.Rev. A, 44, 2558 (1991).
5. G.P.Crawford, D.W.Allender and J.W.Doane, Phys.Rev. A, 45, 8693 (1992).
6. S.A.Różański, R.Stannarius, H.Groothues and F.Kremer, Liquid Crystals, 20, 59 (1996).
7. B.R.Ratna and R.Shashidhar, Mol.Cryst.Liq.Crystals, 42, 185 (1977)

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