

Effect of confinement to porous glass on structure and optical properties of alkylcyanobiphenyls

TAMARA BEZRODNAYA, TATIANA GAVRILKO, IVAN GNATYUK, OLEG YAROSHCHUK,
GALINA PUCHKOVSKAYA

Institute of Physics of NAS Ukraine, 46 Nauki Pr., 03028 Kyiv, Ukraine.

JAN BARAN, HENRYK RATAJCZAK

Institute of Low Temperature and Structure Research Polish Academy of Sciences, ul. Okólna 2,
50-950 Wrocław, Poland.

JAN I. KUKIELSKI

Institute of Experimental Physics, University of Gdańsk, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

The 4-*n*-alkyl-4'-cyanobiphenyls (*n*CB, *n* is the number of carbon atoms in alkyl radical, *n* = 5, 8) confined to porous glasses with four different mean pore sizes (2, 4, 54 and 90 nm) have been studied. Using FT MIR and NIR spectroscopy methods we have investigated the interaction of *n*CB molecules with pore surface. It has been shown that the interaction is accompanied by the formation of hydrogen bonds between SiOH group on the glass pore surface and cyano-group of *n*CB monomer. This is demonstrated by the change in the position and shape of CN stretching and Q(C≡N)+Q(C=C) combination bands in the vibrational spectra of confined *n*CB depending on pore size and the length of alkyl tail. To the contrary, in the case of benzophenone confined to PG, weak π...OH-Si hydrogen bonds are formed.

1. Introduction

Apart from the wide technical applications, porous glasses (PG) are known as suitable host matrices for incorporation of various organic molecules. It is known that confined fluids manifest new interesting physical properties that are absent in bulk materials [1]–[5].

Liquid crystals (LC) are particularly useful as confined fluids because their thermodynamic, optical and electrooptical properties are extremely sensitive to geometric restrictions and surface effect. Although in recent years great success has been achieved in understanding the physical properties of confined liquid crystals [6]–[14], little work has yet been done to characterize the mechanism of interaction of liquid crystal molecules with pore surface on molecular level.

In the present paper we discuss the results of the IR spectroscopic studies of dynamics of some *n*-alkylcyanobiphenyl LCs confined to porous glass cavities of different nominal pore diameter. The aim of the study was to determine the

mechanisms of interaction between the LC molecules and surface active centers of porous matrix and to extract the anchoring conditions from the experimental results.

2. Experimental

2.1. Materials

Porous silicate glass matrices used in our studies were fabricated at the Institute of Technical Chemistry of Martin Luther University of Halle (Germany) from borosilicate glasses using convenient etching technology. They may be described as strongly interconnected and randomly oriented pores with relatively narrow distribution of pore sizes. We used four kinds of PG with nominal pore diameter 2, 4, 54 and 90 nm (PG2, PG4, PG54 and PG90, respectively). The specific pore volume ω and specific surface area S/V for PG2 were: $\omega = 0.14 \text{ cm}^3/\text{g}$ and $S/V = 200 \text{ m}^2/\text{g}$. The samples used were solid plates with flat and parallel surfaces of the dimension of $10 \times 5 \times 0.5 \text{ mm}$.

The 4-*n*-alkyl-4'-cyanobiphenyls (*n*CB, *n* = 5, 8) (Aldrich, U.S.A.), which were used as confined fluids in our studies, are well known LC which exhibit a variety of mesophases with different degree of orientational and translational ordering. Alkylcyanobiphenyls are typical representatives of "soft" materials, and their molecules are built from flexible alkyl tail, rigid biphenyl core and polar cyano-group. The 5CB is the well known representative of nematic LC. Dipole moment μ of the 5CB molecules in ground electronic state determined by spectroscopic method is 6.1D [15], and is mainly located on its CN group. The length of the 5CB molecule is about 2 nm that is comparable with the smallest pore size of our matrices. In addition to *n*CB, benzophenone (commercially available and purified by zone smelting) with $\lambda = 1.9 \text{ D}$, which is an interesting member of the family of aromatic molecules, was used in our studies. Before filling, the PG samples were heated in an oven for 8–10 hours at $T = 400 \text{ }^\circ\text{C}$ and then evacuated in a vacuum line in order to remove physisorbed water. Then the plates were dipped into a melt of filling compound and kept there for 5 hours.

2.2. Methods

Due to the high surface-to-volume ratio of our matrices, we apply convenient transmission IR spectroscopy. Measurements in the MIR region ($400\text{--}4000 \text{ cm}^{-1}$) were performed using Bruker FTIR spectrometer IFS-88 with a resolution of 2 cm^{-1} . The number of scans was 32. The NIR spectra were measured with the help of Cary-5E (Varian) UV-VIS-NIR spectrophotometer in spectral range of $3100\text{--}10000 \text{ cm}^{-1}$ (spectral slit width was 2 cm^{-1}). All measurements were carried out at room temperature.

3. Results and discussion

Figure 1a shows the MIR spectra of empty porous matrices as a function of pore diameter. One can see a transparency "window" between 2000 and 3000 cm^{-1} , which

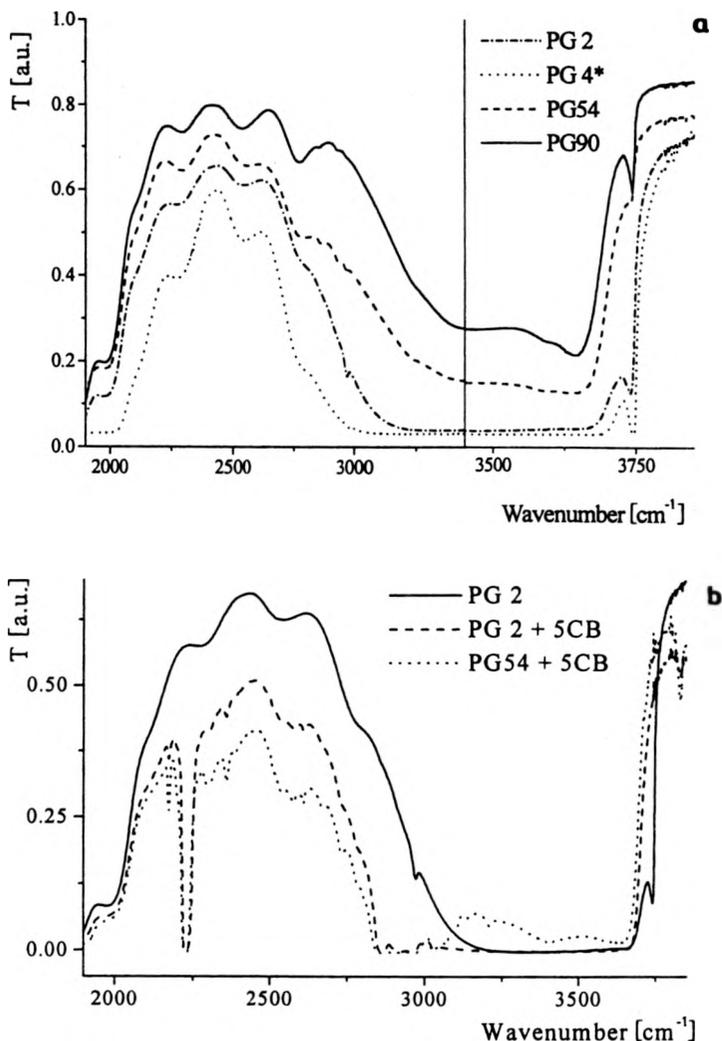


Fig. 1. Fragment of IR spectra of empty PG matrices with different pore diameter (a) and those loaded with 5CB (b) in glass transparency "windows". Vertical line marks the change of the frequency scale.

is limited from the low frequency region by absorption bands of silica framework. On the other hand, strong absorption corresponds to vibrations of hydroxyl groups on the surface of pores. Here broad absorption band ($2700\text{--}3600\text{ cm}^{-1}$) of OH stretching vibrations of associated hydroxyl groups is observed, and a narrow band centered at 3720 cm^{-1} which originates from isolated hydroxyl groups. They are usually regarded as rather strong surface active centers. The assignment of bands to vibrational frequencies of PG matrix can be found in [11].

The MIR spectra of nematic 5CB were studied in detail earlier [16], [17]. The bands in the frequency interval $2800\text{--}3100\text{ cm}^{-1}$ of the spectra correspond to CH stretching vibrations of alkyl tail and benzene ring. In the $1200\text{--}700\text{ cm}^{-1}$ range,

the bands of their deformational vibrations are observed. The intense absorption band centered at 2227 cm^{-1} is assigned to stretching vibration of the cyano-group, and its bandwidth and position are very sensitive to the changes of $n\text{CB}$ phase state [14].

The MIR spectra of 5CB confined to the cavities of PG as a function of pore diameter are shown in Fig. 1b. Let us first consider the changes in the spectra of matrix. In the spectra of filled PG, the bands corresponding to free OH groups on the pore surface become essentially weaker or completely disappear, which is typical of the formation of hydrogen bond [18]. The next important feature of the spectra is the "red-shift" of broad absorption band of associated OH groups. The value of this shift, as derived from the displacement of the low-frequency edge of the band, varies from 30 to 40 cm^{-1} for different matrices.

The changes were also observed in the spectra of the LC. Figure 2a shows that CN stretching band is shifted towards higher frequencies and broadened if the 5CB is confined to PG matrix. The value of this shift increases if pore diameter decreases. Such changes suggest the interaction of CN group with active hydroxyl centers on the pore surface. Since the thickness of our PG matrices did not allow us to perform quantitative studies of CN band in the middle IR region, we studied this band in the near IR spectra. Figure 2b shows the $Q(\text{C}\equiv\text{N})+Q(\text{C}=\text{C})$ combination band ($2226+1606=3832\text{ cm}^{-1}$) of confined 8CB and the results of graphic decomposition of this band using PEAKFIT computer program. In general, the band consists of two Gaussian components. The peak position and the bandwidth of the first band (I) are the same as for pure LC (dipole-dipole bonded dimers). The second band (II) corresponds to $n\text{CB}$ monomer molecules interacting with the pore surface. As one can see from the figure, the contribution of this band is considerable in the case of smaller pore size (PG2) due to the higher surface to volume ratio in such matrices. In the next two cases (PG54 and PG90) this component is very weak. At the same time, the bands corresponding to vibrations of benzene rings and alkyl tail of 8CB molecule do not change their shape or position in the near IR spectra of composition. Therefore, the interaction of CH groups of alkyl tail and benzene ring with the pore surface could be neglected. This is also valid for confined 5CB. Due to specific interaction of CN group with the hydroxyl groups on the surface of PG, the $n\text{CB}$ molecules are forced to be aligned along the surface normal thus providing homeotropic anchoring conditions for the LC. To clear up the role of polar group in alignment of confined molecules, we investigated the system of less polar benzophenone molecules confined to mesoporous PG54. Unlike the case of $n\text{CB}$, in NIR spectra of confined benzophenone, we observed "blue" shift (by $20-50\text{ cm}^{-1}$) of combination bands originated from $q(\text{C}\equiv\text{CH})+\beta(\text{C}\equiv\text{CH})$ and $q(\text{C}\equiv\text{CH})+Q(\text{C}\equiv\text{C})$ vibrations ($3950-4180\text{ cm}^{-1}$ and $4500-4800\text{ cm}^{-1}$, respectively). This suggests that mainly π -electron system of benzene ring is involved in interface interaction of benzophenone molecules with hydroxyl groups on pore surface via weak $\pi\dots\text{OH}-\text{Si}$ hydrogen bonds. This results in planar anchoring conditions for confined benzophenone. It is worth noting that

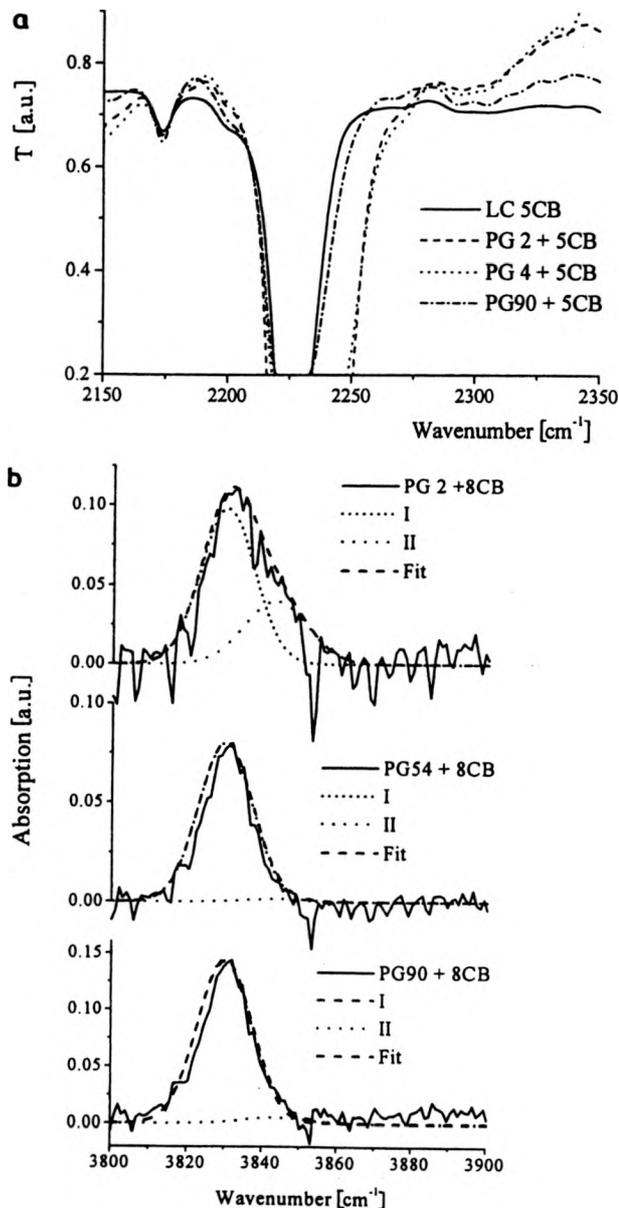


Fig. 2. FTIR absorption spectra of *n*CB confined to PG with different pore diameter: **a** – 5CB in the region of $Q(\text{C}\equiv\text{N})$ stretching vibration, and **b** – 8CB in the region of $Q(\text{C}\equiv\text{N}) + Q(\text{C}\equiv\text{C})$ combination mode.

homeotropic anchoring of *n*CB molecules is not a common feature for all silica surfaces. For example, in the case of interaction of 5CB molecules with dispersed aerosil particles [19], planar anchoring conditions were observed.

Summarizing our results, disappearance of absorption band of "free" OH groups of PG together with the red shift of absorption band of associated OH groups and the shift and broadening of CN stretching vibration band of *n*CB is an evidence of the formation of hydrogen bond. The formation of H-bonds between the CN group of the *n*CB molecule and the hydroxyl groups of the PG of the kind of $-C \equiv N \dots O-H-Si$ provides homeotropic anchoring conditions for liquid crystal at the pore surface. Further investigations of size effect and phase behaviour of confined *n*CB are in progress and will be published in separate paper.

Acknowledgments – The authors are indebted to Dr. T. Morawska-Kowal for her help with measurements of some NIR spectra. J. I. Kukielski gratefully acknowledges financial support from the Polish State Committee for Scientific Research (KBN) within the project BW/5200-5-0300-0. T. Gavrilko would like to thank the Organizing Committee of the *PGL2000 Conference* for financial support.

References

- [1] KLAFTER J., DRAKE J.M., [Eds.], *Molecular Dynamics in Restricted Geometries*, Wiley, New York 1989.
- [2] HURLIMANN M.D., HELMER K.G., DE SWIET T.M., *et al.*, *J. Mag. Res. A* **113** (1995), 260.
- [3] FRITSCHÉ S., HARBERLANDT R., KARGER J., PFEIFER H., *Chem. Phys. Lett.* **242** (1995), 361.
- [4] YIHONG G., LANGLEY K.H., KARASZ F.E., *Phys. Rev. B* **50** (1994), 3400.
- [5] GORBATSCHOV W., ARNDT M., STANNARIUS R., KREMER F., *Europhys. Lett.* **35** (1996), 719.
- [6] CORMA A., *Chem. Rev.* **97** (1997), 2373, and references therein.
- [7] KRALJ S., ZIDANSEK A., LAHAJNAR O., *et al.*, *Phys. Rev. E* **57** (1998), 3021.
- [8] SINHA G.P., ALIEV F.M., *Phys. Rev. E* **58** (1998), 2001.
- [9] SMONDYREV A.M., PELCOVITS R.A., *Liq. Cryst.* **26** (1999), 235.
- [10] AKSNES D.W., GJERDAKER L., KIMTY S., *J. Mol. Struct.* **506** (1999), 297.
- [11] GNATYUK I., PUCHKOVSKAYA G., YAROSHCHUK O., *et al.*, *J. Mol. Struct.* **511–512** (1999), 189.
- [12] ZUBOVA H.-L., KOSSLICK H., CARIUS H.-E. *et al.*, *Microporous Mesoporous Mat.* **21** (1998), 467.
- [13] ZUBOVA H.-L., BENTRUP U., KOSSLICK H., FRICKE R., [In] *Porous Material in Environmentally Friendly Processes. Studies in Surface Science and Catalysis*, Vol. 125, [Ed.] I. Kiricsi, G. Pal-Borbely, J.B. Nagy, H.G. Karge, Elsevier Sci., 1999, p. 321.
- [14] GAVRILKO T., GNATYUK I., PUCHKOVSKAYA G., *et al.*, *Vibrational Spectrosc.* **23** (2000), 199.
- [15] KAWSKI A., KUKIELSKI J.I., *Mol. Cryst. Liq. Cryst.* **182 B** (1990), 209.
- [16] KIROV N., SIMOVA P., *Vibrational Spectroscopy of Liquid Crystals*, Publ. House Bulgarian Acad. Sci., Sofia 1984.
- [17] TORIUMI H., SUGISAWA H., WATANABE H., *Jpn. J. Appl. Phys.* **27** (1988), L935.
- [18] PIMENTEL G.C., MCCLELLAN A.L., *The Hydrogen Bond*, [Ed.] W.H. Freeman and Co., San Francisco 1960.
- [19] PUCHKOVSKAYA G.A., REZNIKOV YU.A. YAKUBOV A.A., *et al.*, *J. Mol. Struct.* **381** (1996), 133.

Received September 18, 2000