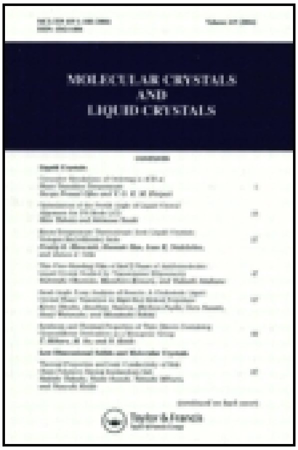

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THE ELECTRONIC ABSORPTION SPECTRA AND MOLECULAR AGGREGATE FORMATION IN VACUUM DEPOSITED FILMS OF MESOGENIC CYANOBIPHENYLS AND THEIR SOLUTIONS

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The Electronic Absorption Spectra and Molecular Aggregate Formation in Vacuum Deposited Films of Mesogenic Cyanobiphenyls and their Solutions

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Electronic absorption spectra of mesogenic 4-pentyl-4'-cyanobiphenyl (5CB), 4-octyl -4'-cyanobiphenyl (8CB) and 4-octyloxy- 4'-cyanobiphenyl (8OCB) films produced by cyanobiphenyl molecular vapor deposition were measured. The appearance of the spectral changes during annealing and dissolution of cyanobiphenyl film samples are discussed assuming molecular dimerization and H-aggregate formation.

Keywords: liquid crystals; condensate films; molecular aggregates

INTRODUCTION

Alkyl and alkoxycyanobiphenyls are widely investigated polar liquid crystals because of their applications in optics and molecular electronic[1]. Molecular dimerization and aggregation of these compounds owing to strong dipole-dipole interactions was studied previously in solutions and vacuum deposited films of cyanobiphenyls by low temperature IR-spectroscopic technique[2,3]. The molecular aggregate formation in liquid crystalline films is important for creation of modern supramolecular materials[4].

In present work the molecular aggregation in condensates films of polar liquid crystals : 4-pentyl-4'-cyanobiphenyl (5CB, $T_{C\text{-}N}$=295K, $T_{N\text{-}I}$=309K), 4-octyl -4'-cyanobiphenyl (8CB, $T_{C\text{-}S}$=293K, $T_{S\text{-}N}$=307K, $T_{N\text{-}I}$=314K) and 4-octyloxy- 4'-cyanobiphenyl (8OCB, $T_{K\text{-}S}$=325K, $T_{S\text{-}N}$=338K, $T_{N\text{-}I}$=352,5K) and their co-condensates with n-decane has been studied by low temperature absorption UV-vis. spectroscopy.

EXPERIMENTAL

Film samples of mesogenic 4-pentyl-4'-cyanobiphenyl (5CB) 4-octyl- 4'-cyanobiphenyl (8CB) and 4-octyl- 4'-cyanobiphenyl (8OCB)of 10-20μm thickness were produced by cyanobiphenyl molecular vapor deposition on the cooled by liquid nitrogen quartz or CaF_2 surfaces using the special spectral vacuum cryostats under the molecular beams conditions. The scheme of cryostat is presented in Figure 1. Cyanobiphenyl vapors were prepared by resistive heating at 110-120 °C. The deposition rate was 10^{15-16} molecules/cm^2 s. The residual pressure in the system did not exceed 0.1Pa.

The cyanobiphenyl - n-decane film samples were obtained by simultaneous co-deposition of CB and n-decane molecules. n-Decane was evaporated at -30 -15 °C and added in 1.5 -10 molar excess.

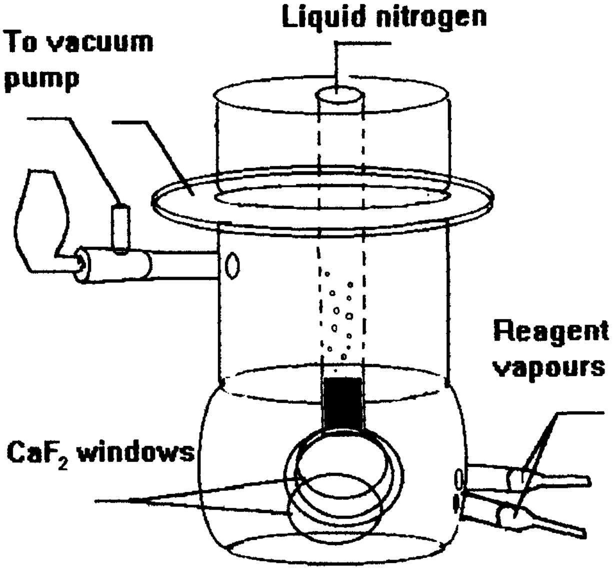

FIGURE1 Schematic diagram of the cryostat for UV-Vis. studies.

The UV-Vis. spectroscopic studies of the samples were carried out *in situ* and *in vacuo* owing to the special construction of cryostat (Figure1) during annealing of the samples up to the room temperatures. The UV-vis. spectra were recorded in transmission mode with a Specord M40 instrument in the region 200-900 nm (50 000 -11 000 cm^{-1}).

RESULTS AND DISCUSSION

In Figure2-4 the absorbtion spectra of vacuum deposited films are presented accordingly for nematic 5CB, smectic 8CB and 8OCB .

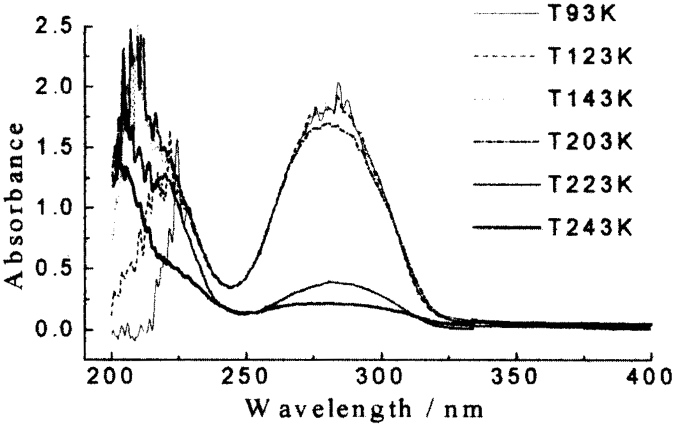

FIGURE 2 Absorption spectra of 5CB film deposited on CaF_2 window at 93K - 1 and during annealing of the film sample at : 2-123K, 3 - 143K, 4 -203K, 5 - 223K, 6-243K.

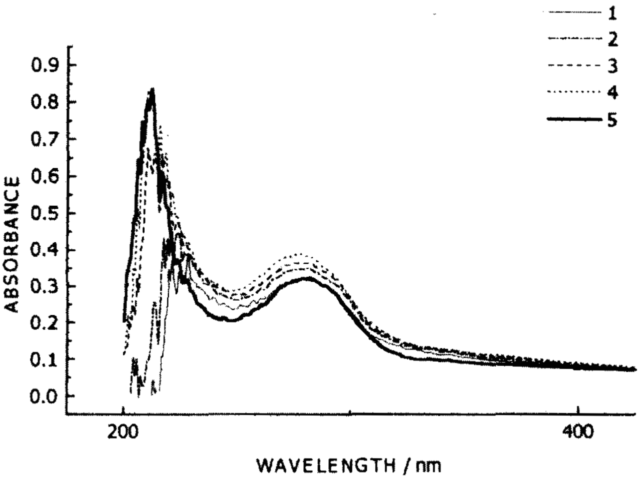

FIGURE 3 Absorption spectra of 8CB film deposited on CaF_2 window at 93K - 1 and during annealing of the film sample at : 2-127K, 3 - 153K, 4 -213K, 5 - 273K.

The UV spectra of alkylcyanobiphenyl films (5CB and 8CB) and alkoxycyanobiphenyl (8OCB) at 93K (Figure 2,3,4 curve 1) consist of two absorption bands near 220 and 280 nm. The assignments of these bands for similar alkyl and alkoxycyanobiphenyls are represented in work[5].

During annealing the film samples, the increase of the absorption at the shorter wavelengths and decrease of the absorption at the longer wavelengths were detected. Blue shifts of the both bands were also observed. The observed spectral changes are probably connected with the CB molecules H-aggregate formation and can be explained by the appearance of the orientation of the transition dipole moments of cyanobiphenyl groups parallel to each other and perpendicular to the stacking direction in the deposited film.

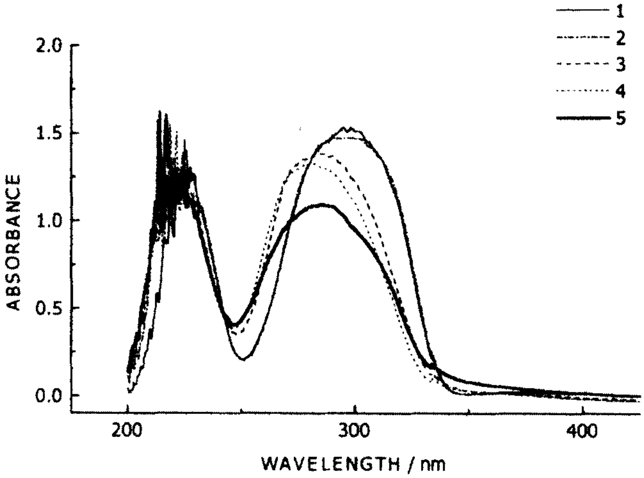

FIGURE 4 Absorption spectra of 8OCB film deposited on CaF_2 window at 93K - 1 and during annealing of the film sample at : 2-183K, 3 - 243K, 4 -273K, 5 - 295K.

The data obtained show that the temperature rise of the cyanobiphenyl film samples leads to the increase of spectral changes due to CB aggregate formation. It could be connected with the growth of general molecular mobility of the system promoted the aggregation processes. H-aggregate formation have been supposed for cyanine dyes[6] solutions and some other cyanophenyl moieties containing systems [7,8].

Blue shifts of the absorption bands near 220 and 280 nm and the increase in their intensity ratio have been larger for 8CB and 8OCB than 5CB. These facts are in agreement with the data obtained in work [6]: the increase in cyanobiphenyl molecule length intensifies the processes of the molecular aggregate formation .

Dissolution of 4-alkyl-4'-cyanobiphenyls by inert hydrocarbon (n-decane), achieved by the simultaneous co-condensation of CB and n-decane molecules, led to the decrease of the spectral changes connected with H-aggregates formation.

CONCLUSIONS

The UV-vis-spectroscopic study of 5CB, 8CB and 8OCB condensate films and their co-condensates with the inert hydrocarbon n-decane was made in temperature range 90-295K. Blue shifts of the absorption bands near 220 and 280 nm and the increase in their intensity ratio were registered during sample heating and the rise in cyanobiphenyl contents in the hydrocarbon (n-decane) matrices.

Acknowledgments

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References

[1] *Handbook of Liquid Crystals*, D. Demus, J.W. Goodby, G.W. Gray, H.W. Spiess, V. Vill (eds), Wiley-VCH, 1998, p. 530.

[2] T.I. Shabatina, T.V. Khasanova, E.V. Vovk, G.B. Sergeev, *Thin Solid Films*, **284/285,** 573 (1996).
[3] T.I. Shabatina, E.V. Vovk, G.N. Andreev, A.Yu. Bogomolov, G.B. Sergeev, *Mol. Cryst. Liq. Cryst.*, **313**, 347 (1998).
[4] , J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives,*Weinheim; New York; Basel; Cambridge; Tokyo; VCH Verlagsgesellschaft mbH, 1995, p. 334.
[5] Hanemann, M.C. Bohm, W. Haase, S.T. Wu, *Liq. Cryst.* **11**, 917 (1992).
[6] I. Scheblikin, Ph.D. Thesises, Moscow Physical-Technical Institute, Moscow, 1999, p. 142.
[7] A. Itaya, T. Imamura, M. Himaguchi, Y. Tsuboi, H. Miyasaka, T. Asahi, H. Masuhara, *Thin Solid Films*, **311**, 277 (1997).
[8] M.D. Everaars, A.T.M. Marcelis, E.J.R. Sudholter, *Langmuir*, **9**, 1986 (1993).