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DETERMINATION OF ORIENTATIONAL ORDER PARAMETER S_2 IN GLASSY LIQUID CRYSTALS BY MEANS OF IR DICHROISM

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ABSTRACT

Nematic liquid crystalline layers have been rapidly solidified and orientational order parameter S_2 in both phases - nematic and glassy ones are calculated and compared.

INTRODUCTION

It is well known that many liquid crystals supercool quite readily. The glassy state of a liquid crystal was first established for cholesteryl hydrogen phtalate(1). A variety of techniques have been used later in the experiments demonstrating the existence of the quenched nematic liquid crystals: X-ray diffraction(2), optical microscopy(3), thermal conductivity(4), adiabatic calorimetry(5), heat capacity(6) and dielectric(7) measurments, NMR(8), nucleation rate theory(9) and recently vibrational spectroscopy(10-12). To describe the state of the quenched liquid crystals a new term "glassy liquid crystal" has been suggested(6,12). However, no quantitative arguments have been presented up to now in order to demonstrate whether the resultant glass retains the liquid crystal alignment or not. A very useful evidence could be the comparison of the orientational order parameter S_2 in both phases.

IR dichroitic ratio was applied succesfully for the investigation of S_2 temperature dependence in different liquid crystals: di-n-alkoxyazoxybenzenes(13), p,n-alkoxybenzoic acids(14), 2,4-nonadiene, 2,4-decadiene and 2,4-undecadiene acids(15), p-cyanobenzylidene p,n-octyloxyaniline(16), N-(p-ethoxybenzylidene)-p-butylaniline(17) in their nematic and smectic A phases. Recently, we reported S_2 temperature dependence for some p-alkoxybenzylidene cyananilines and N-(p-alkoxybenzylidene)-p-butylanilines by IR absorption spectroscopy(18). However, no determination of the orientational order parameter in the glassy liquid crystal has been made up to now.

The chief purposes of the present experiment are to ascertain quantitatively a) the correctness of the claim that both the molecular distribution and the director alignment are maintained during a liquid nitrogen quench and b) whether the rapidly solidified nematic layer retains the macroscopic liquid crystalline order.

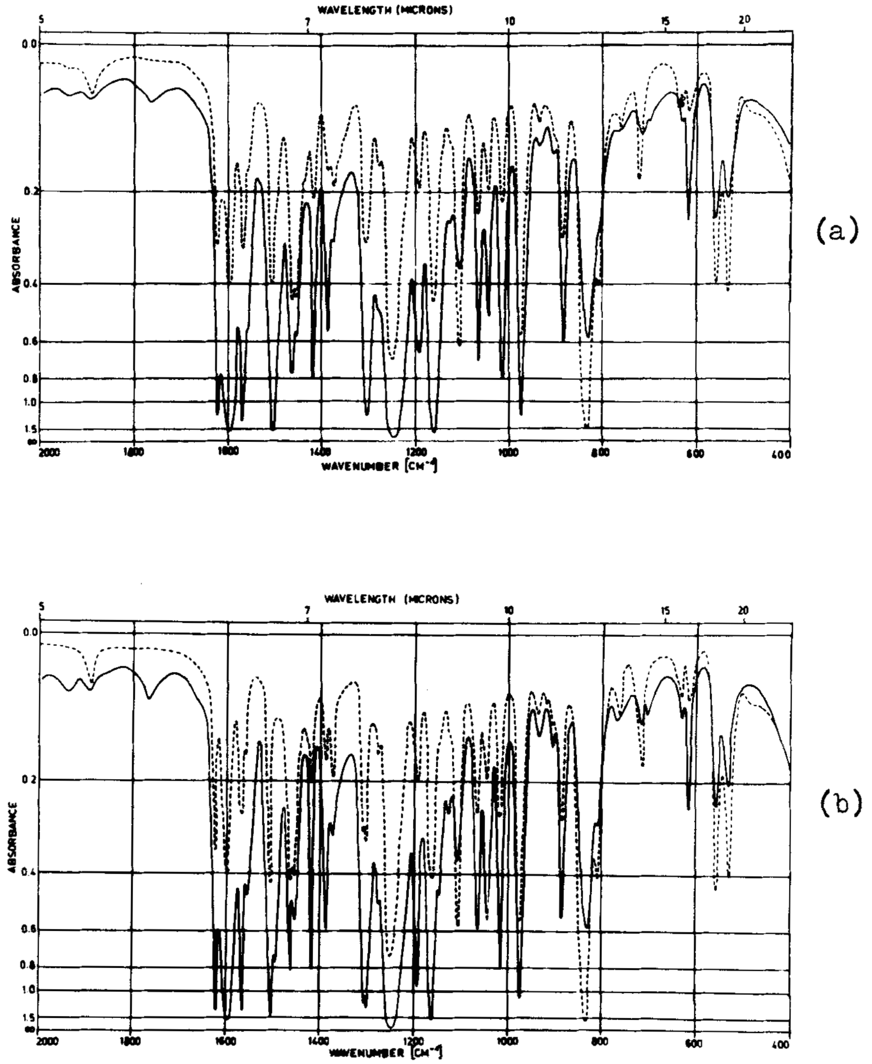
RESULTS AND DISCUSSION

The nematic liquid crystals N-(p-methoxybenzylidene)-p-butylaniline (MBBA), N-(p-ethoxybenzylidene)-p-butylaniline (EBBA) and N-(p-propoxybenzylidene)-p-pentylaniline (PBPA) have been used for our experiments. The liquid crystal molecules are aligned homogeneously by rubbing. The polarized IR spectra are recorded at the beginning of temperature interval of the mesophase existence - 295 K (MBBA), 313 K (EBBA) and 308 K (PBPA). The quenching with a rate - 15 K min^{-1} began also from the same temperatures. The spectrophotometer Perkin-Elmer 621 provided with wire grid polarizer was used for the registration of the polarized IR spectra in the region 4000 - 400 cm^{-1}. The temperature controller TEM-1C maintained automatically the temperature below and above the ambient. Using a homogeneously aligned sample and polarized radiation S_2 can be evaluated by the ratio R between the two absorption coefficients $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, the subscript $\parallel$ and $\perp$ denote respectively the case when the incident radiation is polarized parallel and perpendicular to the direction of the sample alignment. If the transition moment is parallel to the long molecular axis (symmetry type A_1) we can write down(19):

$$S_2 = (R - 1)/(R + 1). \qquad (1)$$

If the vibrational transition moment is perpendicular to the long axis (symmetry type B_2) we have:

$$S_2 = (1 - R)/(1 + 2R). \qquad (2)$$



<u>FIGURE 1</u> IR spectrum of PBPA (12 m thick film) at: (a) 308 K and (b) 90 K; full line - E //n; dash line - E⊥n.

As one can see from Fig. 1 (a,b) where the polarized IR spectra of PBPA in its nematic and glassy liquid crystal state are reported there are not well pronounced IR bands, strong and distinct, not overlapped by its neighbours and with known direction of their transition moments as, for example, CN stretch vibration(18). However, the assignments given in (20) can help us to choose some bands, suitable for S_2 calculations. The investigated molecules can be assigned to C_s point group. If, in the normal coordinate analysis we consider a mode for which from the potential energy distribution is known that it has a component greater than 50% to be a characteristic group frequency, only eight normal modes between 4000 and 400 cm^{-1} can be used for the S_2 determination. Seven of them are polarized parallel to the long axis (symmetry type A_1) and one - that at 840 cm^{-1} (symmetry type B_2) has a transition dipole moment perpendicular to the long axis. For the determination of S_2 we choose six bands: 1165 cm^{-1} - S_8 (A_1) + S_9 (A_1), 1417 cm^{-1} - S_{19} (A_1) + S_9 (A_1), 1505 cm^{-1} - S_{20} (A_1) + S_{19} (A_1), 1567 cm^{-1} - S_8 (A_1) + S_7 (A_1) + S_9 (A_1), 1595 cm^{-1} - S_8 (A_1) + S_7 (A_1) + S_9 (A_1) and 1625 cm^{-1} - CH=N stretching and phenyl ring-N S_8 (A_1). The results for S_2 in the nematic and in the glassy liquid crystal phase at 90 K and at every 40 degrees during the freezing process averaged on all six bands are summarized in Table 1.

Saupe and Maier(21) have pointed out that the evaluation of orientational order parameter from dichroic studies must include appropriate corrections for the anisotropy in the refractive indices

TABLE 1 Orientational order parameter S_2 in the nematic and in the glassy liquid crystal phase.

Materials / T K	MBBA	EBBA	PBPA
nematic liquid crystal			
295	0.46		
313		0.55	
308			0.49
glassy liquid crystal			
203	0.42	0.52	0.47
163	0.45	0.51	0.41
123	0.45	0.55	0.47
90	0.40	0.50	0.48

and the polarizability of the liquid crystal medium. They show that when a homogeneously aligned sample is used, the resultant systematic correction to S_2 can amount to as much as 10%. In the literature, however, are not available data for $n_{//}$ and $n_{\perp}$ in the IR region for investigated by us samples and as a result the so-called "Lorenz inner field correction" has not been done. That's why the present study leads only to relative values of S_2.

As one can see from the table the S_2 values of both phases - nematic and glassy liquid crystals are in the limits of error equal and do not change during the quenching process.

CONCLUSION

The transition of the nematic liquid crystal to a glass with nematic order upon quenching has been confirmed quantatively. Furthermore, it has been shown that in spite of the thermal shock the macroscopic alignment continues to operate effectively throughout the whole process.

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