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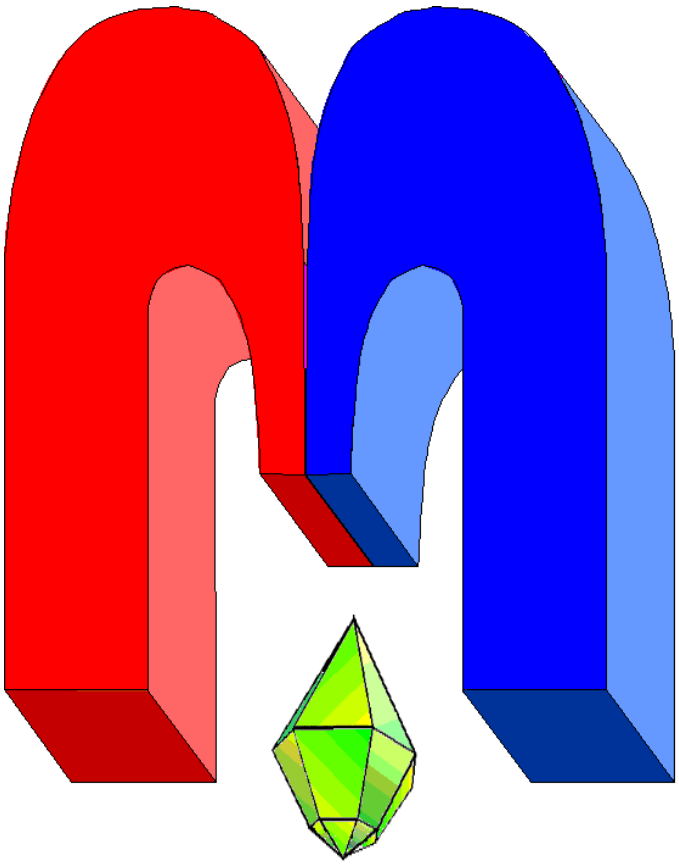

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Spin probe orientation distribution functions in aligned nematic liquid crystal

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Orientation distribution functions of nitroxide spin probe in nematic liquid crystal 5CB embedded into porous polyethylene film were determined at 295 K and at 77 K by numerical simulation of electron paramagnetic resonance (EPR) spectra. The procedure of simulation of EPR spectra at 77 K in the absence of molecular mobility of spin probe molecules allows determination of non-equilibrium orientational distribution function in supercooled liquid crystals. The suggested procedure yields an orientation distribution function of orientational axis of a spin probe molecule. Orientation distribution functions for the sample at 295 K and 77 K were found to be similar.

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1. Introduction

Spin probe method is widely used for investigation of alignment and rotational mobility of liquid crystals [1-3]. This method is based on analysis of EPR spectra of spin probes – nitroxide radicals introduced into liquid crystalline media.

Characteristic of orientational ordering is an orientation distribution function (ODF). It shows a fraction of particles oriented in angle interval ($\alpha + d\alpha$, $\beta + d\beta$, $\gamma + d\gamma$). A method for determination of an orientation distribution function of spin probes was developed previously [4]. ODF is expanded in a series of spherical harmonics:

$$\rho(\beta,\gamma)=\sum_{l=0}^{\infty}\left(\frac{1}{2}a_{l0}P_l(\cos\beta)+\sum_{k=1}^{l}P_{lk}(\cos\beta)\left[a_{lk}\cos k\gamma+b_{lk}\sin k\gamma\right]\right). \quad (1)$$

Here $P_l(\cos\beta)$ are Legendre polynomials, $P_{lk}(\cos\beta)$ are associated Legendre functions.

Angles (β, γ) relate g-tensor frame of a spin probe molecule with a sample frame. Expansion coefficients a_{lk}, b_{lk} are determined via numerical simulation of EPR spectra. ODF expressed as Eq. (1) corresponds to distribution of orthorhombic spin probes in an axial sample. In the most general case an ODF depends on three angles (α, β, γ). The method [4] is used for investigation of alignment in frozen media, in the absence of molecular mobility.

The most widespread approach for investigation of ordered media by EPR spectroscopy implies rotational diffusion of a spin probe in a field of an orienting potential $U(\alpha, \beta, \gamma)$, which is created by an orienting media (see Chapter 1 in [1]). However this approach is not optimized for investigations of orientation distribution of molecules in samples in the absence of molecular mobility. The orientation distribution function in this case is presented as a Boltzmann's exponent:

$$\rho(\alpha,\beta,\gamma)=\frac{e^{-U(\alpha,\beta,\gamma)/k_bT}}{\int e^{-U(\alpha,\beta,\gamma)/k_bT}d\alpha d\beta d\gamma}. \quad (2)$$

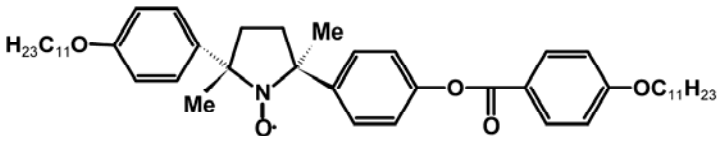

Figure 1. Spin probe 2,5-dimethyl-2-undecyloxyphenyl-5-[4-(4-undecyloxybenzene-carbonyloxy)phenyl]-pyrrolidine-1-oxide

Within this approach the orientational axis of spin probe molecule is assumed to coincide with one of the axes of rotational diffusion tensor. The orienting potential is expanded in a series of spherical Wigner's *D*-functions:

$$\frac{U(\alpha,\beta,\gamma)}{k_bT} = \sum_{l,m,k} \varepsilon^l_{mk} D^l_{mk}(\alpha,\beta,\gamma). \tag{3}$$

Potential expansion coefficients and coefficients of rotational diffusion are sought for parameters of numerical simulation of EPR spectra.

In this work we combine these two approaches to determine orientation distribution functions of spin probes in a liquid crystalline media at conditions of presence and absence of rotational mobility.

2. Sample preparation

Liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB) from Sigma Aldrich was used without further purification. Nematic phase was found within temperature interval 295-308 K.

Stretched porous polyethylene (PE) films were produced by the procedure described in [5]. The material was kindly granted by Prof. G.K. Elyashevitch (Institute of Macromolecular Compounds, RAS). Pores of this material with diameter ~200 nm are elongated mainly uniaxially. This material aligns liquid crystals embedded in it due to the action of internal surface of the pores [6].

Stable nitroxide radical 2,5-dimethyl-2-undecyloxyphenyl-5-[4-(4-undecyloxybenzene-carbonyloxy)phenyl]-pyrrolidine-1-oxide R (Fig. 1), was synthesized as described elsewhere [7] and kindly granted by Prof. R. Tamura (Kyoto University). The concentration of the spin probe introduced into 5CB was less than 10^{-3} M to avoid dipole-dipole broadening of EPR spectrum lines. This nitroxide radical has rigid central core. It has been shown earlier [8] that being introduced into oriented liquid crystalline media, this spin probe exhibits rather strong angular dependence of EPR spectrum. Hence it is a promising orientation-sensitive spin probe.

The liquid crystal with admixture of the spin probe was readily soaked into the film due to the surface tension. Then ten layers of filled film were stacked and co-aligned to form the sample.

3. EPR spectra numerical simulation. Determination of orientation distribution function

EPR spectra recorded at different angles between magnetic field vector and the sample anisotropy axis were simulated jointly. The procedure for numerical simulation of EPR spectra in the absence of molecular mobility is described in detail in [4]. We have modified the procedure to determine the orientation distribution of the axis of a spin probe, which is ordered to the maximum extent (orientational axis). In this case ODF depends on one angle and can be expanded in a series of Legendre polynomials:

$$\rho(\beta') = \sum_l \frac{1}{2} c_l P_l(\cos\beta'). \tag{4}$$

It was proved that expansion parameters c_l are related with expansion parameters a_{lk}, b_{lk} of expansion (1) through Eqns. (5):

$$a_{lk} = c_l \frac{(-1)^k (l-k)!}{(l+k)!} \cos k\varphi \, P_{lk}(\cos\theta), \qquad b_{lk} = -c_l \frac{(-1)^k (l-k)!}{(l+k)!} \sin k\varphi \, P_{lk}(\cos\theta). \tag{5}$$

Sought for parameters of this procedure are expansion coefficients c_l of the ODF of the spin probe orientational axis and angles (θ, φ), which relate orientational axis of the spin probe with *g*-tensor principal axes.

To take into account rotational mobility of spin probes in ordered media within Brownian diffusion approach, we used a procedure suggested in [9]. Orientation distribution is expressed as a function (2), sought for parameters of numerical simulation are expansion coefficients of an orienting potential (3), rotational diffusion coefficients and angles which relate principal axes of diffusion tensor and principal axes of *g*-tensor of the spin probe (θ', φ').

4. Results and discussion

EPR spectra of the spin probe in 5CB embedded into porous PE film recorded at 77 K and at 295 K are shown in Fig. 2. The difference between them is accounted for rotational mobility of the spin probe molecules at 295 K.

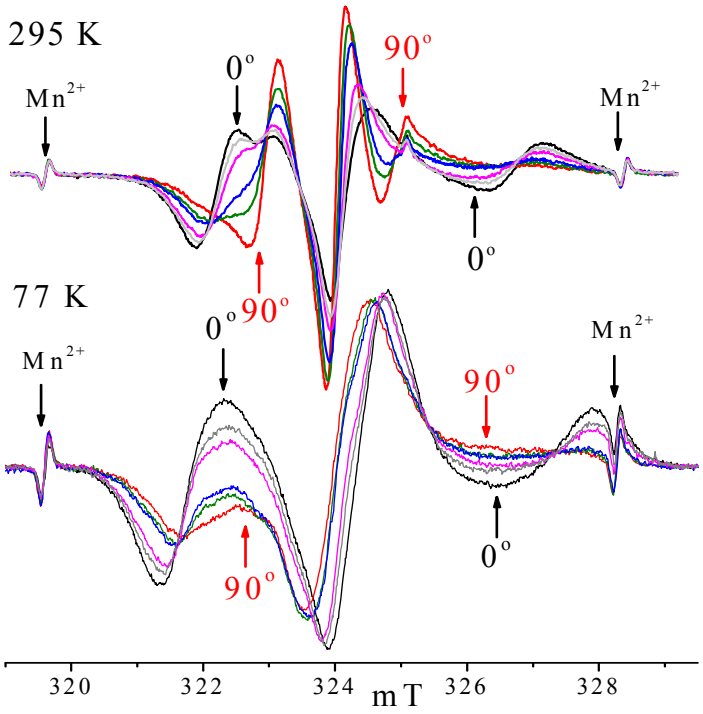

Figure 2. EPR spectra of spin probe R in liquid crystal 5CB embedded into porous PE film recorded at different angles between the sample anisotropy axis and magnetic field. EPR frequency is 9.8 GHz.

Orientation distribution function of the spin probe at 77 K is shown in Fig. 3. The ODF shows distribution of medium director in *g*-tensor frame of probe molecule. Angles (θ, φ) show tilt of orientational axis of the molecule relative to *g*-tensor frame.

If equilibrium is achieved at any temperature, then in accordance with Eq. (3), orienting potential expansion coefficients go up with decreasing of temperature. It means that orientational distribution of the spin probes at 77 K should be more anisotropic, than at 295 K. However, our experiments have not validated this statement. To compare ODF at 295 K and at 77 K we expanded ODF determined at 295 K, expressed via Eq. (2) in a series of spherical harmonics. The first coefficients of the series and values of order parameters are presented in Tab. 1. Order parameter is $F = \langle P_2 \rangle = c_2/5$, where angle parentheses mean averaging over all particles. Taking into account the values of coefficients obtained for ODFs at 295 K and 77 K, one can conclude that ODFs at 295 K and at 77 K are rather similar. Only slight increasing of order parameter F with decreasing of temperature takes place. Therefore, molecular orientation distribution at 77 K approximately corresponds to nematic liquid crystalline state at room temperature. It means that rapidly cooled liquid crystal is in non-equilibrium supercooled state. Orientational characteristics of molecules in cooled liquid crystal

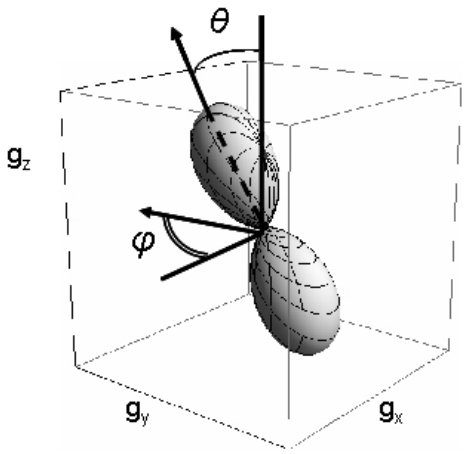

Figure 3. Orientation distribution function (77 K) of spin probe R in 5CB embedded into porous PE film

Table 1. ODFs parameters

	77 K	295 K
c_2	2.48 ± 0.12	2.24 ± 0.10
c_4	0.76 ± 0.87	1.17 ± 0.10
c_6	-	0.36 ± 0.04
F	0.50 ± 0.02	0.42 ± 0.02
	$\theta = (32 \pm 1)^o$	$\theta' = (38 \pm 1)^o$
	$\varphi = (90 \pm 9)^o$	$\varphi' = (90 \pm 18)^o$

do not meet condition of Boltzmann's equilibrium (2) that lies in the base of the approach (see Chapter 1 in [1]).

Angles (θ', φ'), which relate diffusion frame and *g*-tensor frame, determined at 295 K were found to be in qualitative agreement with angles (θ, φ) which give direction of orientational axis of the spin probe in *g*-tensor frame, determined at 77 K (see Tab. 1). The vicinity of orientational axis and principal axis of rotational diffusion for this spin probe is accounted for rodlike shape of the molecule.

The reported procedure of numerical simulation of EPR spectra of spin probes in the absence of rotational mobility allows one model-independent determination of orientation distribution function.

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