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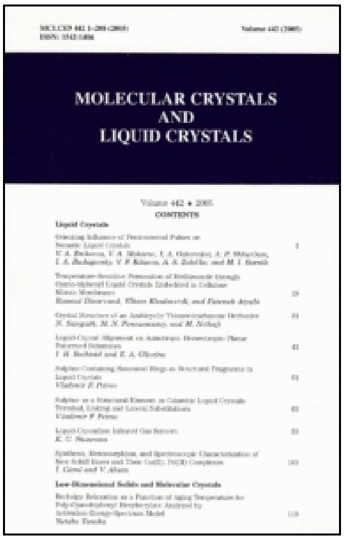

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The Novel Stable Nitroxide Radicals as Perspective Spin Probes for Study of Orientation Order of Liquid Crystals and Polymers

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The Novel Stable Nitroxide Radicals as Perspective Spin Probes for Study of Orientation Order of Liquid Crystals and Polymers

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Stable nitroxide radicals with rigid core were used as spin probes for investigation of orientational order of nematic liquid crystals MBBA and 5CB, uniaxially stretched polyethylene and porous polyethylene. The orientation distribution functions of probe molecules were determined. The order parameters of the true orientation axes were estimated. It was demonstrated that the novel nitroxide radicals show orientational alignment of both liquid crystals and polymers more effectively than ordinary spin probes.

Keywords EPR; liquid crysrals; orientation; polymers; spin probes

1. Introduction

As it is well known, many properties of liquid crystals and strained polymers are dictated by the alignment of their molecules. The most comprehensive characteristic of molecular order is an orientation distribution function (ODF) that presents the fraction of particles oriented in a certain direction. There is a method now for determination of ODF of paramagnetic particles ordered in the sample. The method is based on the numerical analysis of EPR spectra angular dependence of paramagnetic additives (spin probes) [1–3]. By means of determination of the orientational order of spin probe one can obtain information about alignment of the matrix molecules. As it was shown earlier [2,3] the method demonstrates a high structure sensitivity.

Choice of a spin probe is very important as far as geometry of the probe molecules, its interaction and complexation with the matrix molecules influence heavily on the molecular alignment of probes. Piperidine nitroxide radicals (TEMPO, TEMPOL, TEMPON) are commonly used spin probes. The aim of the present work is investigation of orientational order of the novel stable nitroxide radicals 2,5-dimethyl-2-alkyloxyphenyl-5-[4-(4-alkyloxybenzenecarbonyloxy)phenyl]-pyrrolidine-1-oxides.

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These radicals have rigid central moiety and they are able to form nematic and smectic mesophases as individual substances [4]. We suppose that these spin probes have high capability of embedding into liquid crystalline matrices.

2. Experimental

2.1. *Materials*

The novel nitroxide radicals were synthesized as described elsewhere [4–6] and were kindly granted by Prof. R. Tamura (Kyoto University). We used spin probes with three different alkyl substituents: butyl, undecyl and pentadecyl. Below we refer to these spin probes as Ra, Rb and Rc correspondingly. Molecules of these spin probes have two chiral centers - atoms C_2 and C_5 of the pyrrolidine ring. We used both enriched with (2S,5S)-enantiomer (>85.2%) and racemic mixtures. The spin probe TEMPOL (2,2,6,6-tetramethyl-4-hydroxopiperidine-1-oxide) from Sigma Aldrich was used without further purification. The structures of used spin probes are shown in Figure 1.

Nematic liquid crystal *N*-(4-Methoxybenzylidene)-4-butylaniline (MBBA) (*Aldrich*, 98%) was purified by distillation at 0.133 Pa. The clearing point temperature of purified MBBA was found to be 317 K. According to the references [7,8] its clearing point is within the range 316–321 K. Nematic mesophase exists in the range 293–320 K [9]. Nematic liquid crystal 4-n-pentyl-4′-cyanobiphenyl (5CB) from *Merck* was used without further purification. It forms mesophase within the range 295–308 K [10].

High density polyethylene (HDPE) films with thickness of 0.2 mm were kindly granted by Prof. A.V. Efimov (Moscow State University). Stretched porous polyethylene (SPPE) films with thickness of 0.05 mm were produced by extrusion followed by annealing and uniaxial stretching. SPPE films were kindly granted by Prof. G.K. Elyashevitch (Institute of Macromolecular Compounds, RAS) [11]. Pores of this material with ~200 nm diameter are elongated mainly uniaxially. This porous polyethylene aligns liquid crystals embedded in it due to the action of pores internal surface [12–14].

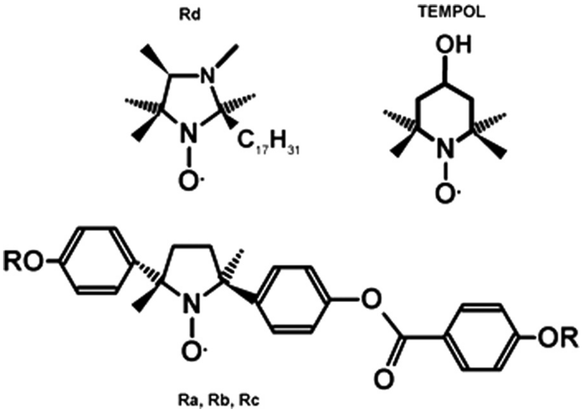

Figure 1. Structures of the spin probes. Nitroxides TEMPOL and 2,5-dimethyl-2-alkyloxyphenyl-5-[4-(4-alkyloxybenzenecarbonyloxy)phenyl]-pyrrolidine-1-oxides (Ra – alkyl is C_4H_9, Rb – alkyl is $C_{11}H_{23}$, Rc – alkyl is $C_{15}H_{31}$) were used in the present paper, spin probe 2-heptadecyl-2,2,3,4,5-pentamethylimidazoline-1-oxide (Rd) was used in [15].

2.2. *Sample Preparation*

To study liquid crystal aligned by magnetic field, quartz ampoule for ESR measurements was filled with liquid crystal containing spin probe (ampoule diameter was 3 mm, sample height was 10 mm, spin probe concentration was about $1 \cdot 10^{-3}$ mol/l). The sample was exposed to 0.3 T magnetic field of ESR spectrometer at 295 K for 5 minutes and then was rapidly cooled down to 77 K in the magnetic field. In this way the aligned sample with symmetry axis ordered perpendicular to the ampoule axis was produced. It was confirmed by special experiments that ordering of both MBBA and 5CB reaches the saturation in the field of 0.3 T. It was checked as well that the alignment of the liquid crystals remains constant at 77 K within the time of the experiment (several hours).

To study liquid crystal alignment in SPPE pores, 5CB liquid crystal containing spin probe was deposited on the SPPE film surface. The liquid crystal was readily soaked in the SPPE film by the action of pores surface. Then 10 layers of filled film were stacked up and co-aligned to form the sample.

To study stretched HDPE alignment, the solution of spin probe in benzene was deposited on the surfaces of two pieces of HDPE. After solvent evaporation the films were stuck together by heating at 369 K. After that the sample was stretched in 5 times at 295 K. Then six layers of stretched film were stacked up as described above.

2.3. *EPR Spectra*

EPR spectra were recorded with X-band ESR spectrometer Varian E3 at 77 K. The sample was placed into Dewar vessel filled with liquid nitrogen. EPR spectra were recorded at different angles between the sample anisotropy axis and the magnetic field vector with 10° step. Turn angle was set up using goniometer with accuracy ±2°.

2.3.1. *EPR spectra simulation.* Least-squares numerical simulation of EPR spectra was performed according to the method described earlier [2]. Since all samples under consideration have uniaxial symmetry, the ODFs of paramagnetic particles were expressed as a series of spherical harmonics:

$$\rho(\beta,\gamma) = \sum_{j=0}^{\infty}\left[\frac{1}{2}a_{j0}P_j(\cos\beta) + \sum_{k=1}^{j}P_j^k(\cos\beta)(a_{jk}\cos(k\gamma) + b_{jk}\sin(k\gamma))\right] \qquad (1)$$

where P_j – Legendre polynomials, P_j^k – associated Legendre functions, angles β, γ characterize orientation of the sample symmetry axis in magnetic reference frame of the probe molecule.

The numerical simulation was performed in two steps. At first step the magnetic parameters of the radicals (values of g-tensors and hyperfine structure (HFS) tensors) as well as shape and width of individual resonance line were obtained by means of simulation of EPR spectrum of the disordered sample. After that, simulation of EPR spectra angular dependences of the aligned sample was used for determination of the ODF.

There is a special direction in the probe reference frame, which is oriented in the ordered material to the maximum extent. This direction is defined by geometry of paramagnetic molecule, its interaction and complexation with the matrix molecules. Below we refer this direction as the true orientation axis of the radical. The true orientation axis in general does not coincide with any of magnetic axes. In the present work we have determined order parameters of the true orientation axes and their positions in the spin probes reference frames for all systems under consideration.

3. Results and Discussion

The EPR spectra of radical Ra in liquid crystal MBBA aligned by magnetic field are presented in Figure 2(a). These spectra have been recorded at various angles between the sample symmetry axis and the magnetic field vector. One can see that paramagnetic molecules are ordered in the sample jointly with liquid crystal molecules. In Figure 2(b) one can see the result of mutual computer simulation of these experimental spectra. The expansion coefficients of ODF in series (1) were determined as a result of the simulation. Commonly the main axes of g- and HFS-tensors of nitroxide radicals coincide. In this case eight different spin probe orientations in the sample corresponding to angles (β, γ), $(\beta, -\gamma)$, $(\beta, \pi+\gamma)$, $(\beta, \pi-\gamma)$, $(\pi-\beta, \gamma)$, $(\pi-\beta, -\gamma)$, $(\pi-\beta, \pi+\gamma)$, $(\pi-\beta, \pi-\gamma)$ are indistinguishable in EPR spectra, i. e. ODF also has orthorhombic symmetry. As a result, in the series (1) only coefficients a_{l0} and a_{lk} with even l and k are non-zero, and all of b_{lk} are zero. The obtained coefficients for various spin probes in different matrixes are shown in Table 1. Value a_{00} is defined by number of paramagnetic molecules in the sample, for normalized function it is equal to one.

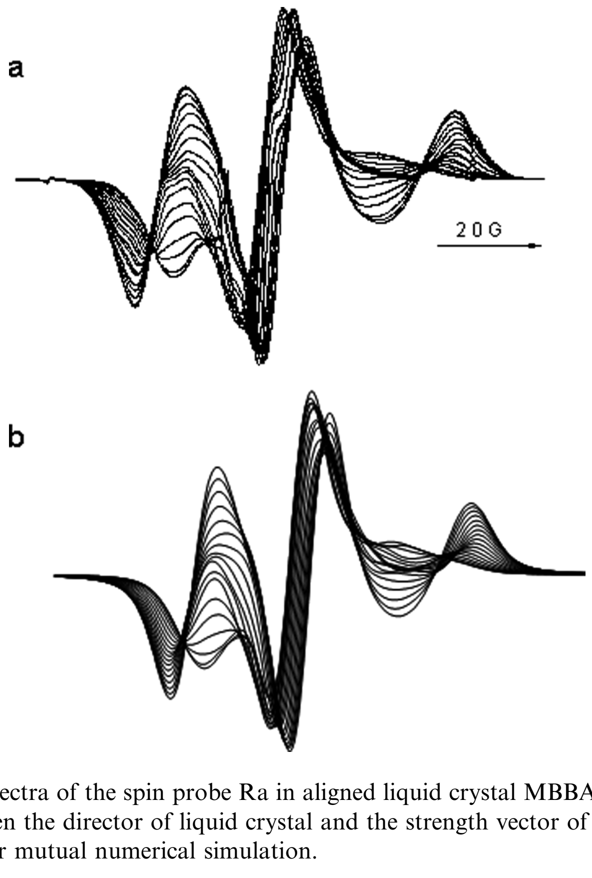

Figure 2. EPR spectra of the spin probe Ra in aligned liquid crystal MBBA recorded at various angles between the director of liquid crystal and the strength vector of magnetic field (a) and result of their mutual numerical simulation.

Table 1. The expansion coefficients of orientation distribution functions of various spin probes in liquid crystals and polymer matrices; the order parameters of true orientation axes and the Euler angles characterizing positions of these axes in magnetic reference frame of the spin probe

	a_{20}	a_{22}	a_{40}	a_{42}	a_{44}	a_{60}	a_{62}	a_{64}	a_{66}	F_{true}	β_{true}	γ_{true}
Ra/MBBA	2.06	−0.121	−0.40	−0.085	~0	−1.06	−0.024	~0	~0	0.70	32	~0
Rb/MBBA	2.14	−0.117	−0.56	−0.092	~0	−1.32	−0.031	~0	~0	0.70	32	~0
Rb/5CB	1.91	−0.133	0.11	−0.065	~0	−0.70	−0.024	~0	~0	0.63	30	~0
Rb/5CB/SPPE	1.37	−0.15	0.25	−0.022	~0					0.55	30	~0
Ra/HDPE	0.815	−0.029								0.26	29	~0
Rb/HDPE	1.425	−0.106	0.37	−0.018	0.0016					0.40	31	~0
Rc/HDPE	2.422	−0.103	1.06	−0.056	0.0011	0.144	−0.0016	~0	~0	0.68	24	~0
Rd/HDPE	0.488	−0.056	0.216	−0.010	~0							
TEMPOL/MBBA	0.23	−0.058	0.019	−0.017	~0							

The ODF of radical Ra in liquid crystal MBBA aligned by magnetic field is presented in Figure 3(a). This function shows the orientation of the sample symmetry axis in the radical magnetic frame. The positions of g-tensor main axes in the nitroxide fragment are presented in Figure 3(b). In the case under consideration axes g_x are oriented predominantly perpendicular to the sample symmetry axis, while magnetic axes g_y and g_z make angles 58° and 32° with the symmetry axis, correspondingly. From ODF expansion coefficients one can calculate the order parameters of the radical magnetic axes which present average orientation of these axes relative to the sample symmetry axis $F = 1/2(\langle 3\cos^2\theta\rangle - 1)$:

$$F_x = -a_{20}/10 + 6a_{22}/5, \tag{2a}$$

$$F_y = -a_{20}/10 - 6a_{22}/5, \tag{2b}$$

$$F_z = a_{20}/5, \tag{2c}$$

where F_x, F_y and F_z – order parameters of g_x, g_y and g_z axes, correspondingly.

In the case under consideration the most significant value, which reflects the extent of the probe ordering is order parameter of axis g_x. The value of order parameter for axis g_x ($F_x = -0.35$) shows that these axes are ordered perpendicularly to the director of liquid crystal to a great extent (the F_x value for perfect perpendicular orientation is -0.5). The values of order parameter for axes g_y and g_z ($F_y \approx 0$, $F_z = 0.41$) reflect not only the extent of order but also arrangement of these axes relative to the sample symmetry axis. The order parameter for the true orientation axis F_{true} was determined for a more exact description of the extent of spin probe alignment [3]. This values was $F_{true} = 0.70$. The values of Euler angles which show the direction of the true orientation axis in the magnetic frame of probe were found to be $\beta_{true} = 32°$, $\gamma_{true} \sim 0°$.

ODFs of radicals Rb and spin probes TEMPOL in liquid crystal MBBA aligned by magnetic field, radicals Rb in liquid crystal 5CB aligned by magnetic field and aligned by the pores of SPPE, radicals Ra, Rb, Rc in stretched HDPE were obtained similarly. The expansion coefficients of ODFs in series (1) as well as the true order

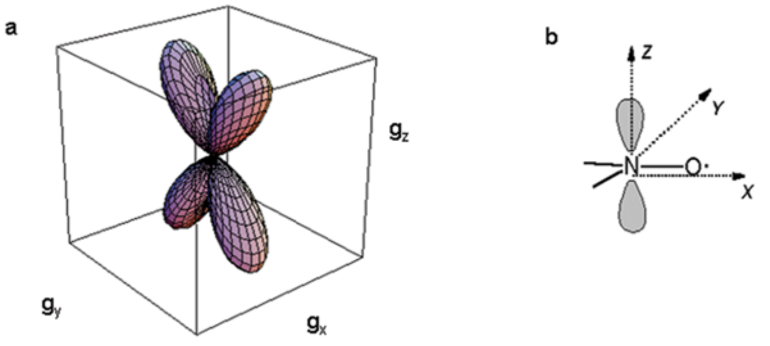

Figure 3. The orientation distribution function of radicals Ra in aligned liquid crystal MBBA. The positions of g-tensor main axes in nitroxide fragment (insert). (Figure appears in color online.)

parameters and angles $\beta_{true},\gamma_{true}$ are presented in Table 1. It was found that ODF of spin probe R enriched by (2S, 5S)-enantiomer coincides with ODF of racemic mixture of spin probe R.

One can see that the ODF expansion coefficients for the probe Rb in MBBA are very close to the corresponding coefficients for probe Ra. Thus, orientation distribution of radicals R does not depend on the alkyl substituent length.

The ODF of TEMPOL in liquid crystal MBBA is presented in Figure 4(a). This function is described by coefficients with $j = 2$, 4 in series (1) only. The extent of order for TEMPOL in MBBA is less then for radicals Ra and Rb. Hence, the novel spin probes reflect liquid crystalline alignment more efficiently than commonly used spin probes.

In Figure 4(b) one can see the ODF of radical Rb in liquid crystal 5CB aligned by magnetic field. It is similar to the function for this radical in MBBA. The directions of the true orientation axes are the same in these two cases. As it was estimated in [3] the direction of the true orientation axis of Rb in 5CB is very close to the position of the main axis of the rotational diffusion. The true order parameter for Rb in 5CB is a little smaller then for Rb in MBBA, so the ordering action of liquid crystal 5CB to spin probe Rb is less then action of liquid crystal MBBA.

One can see that shape of the ODF of radicals Rb in liquid crystal embedded in pores of SPPE differs from shape of the ODF of Rb in liquid crystal aligned by magnetic field (Figure 4b, c). But more rigorous examination has revealed that both functions consist of four "petals" and the directions of these petals are the same. Indeed, the angles $\beta_{true},\gamma_{true}$ are close in these two cases. The difference between the functions consists in extent of their ordering. The true order parameter in the

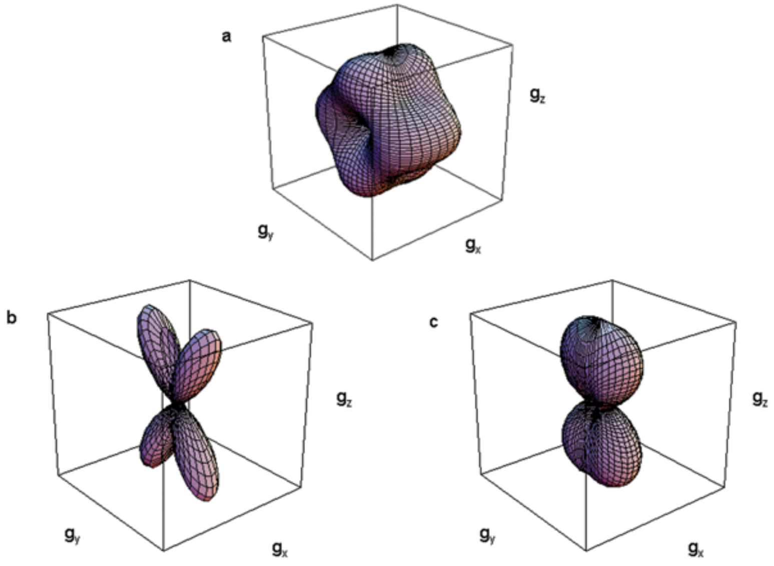

Figure 4. The orientation distribution functions of radicals TEMPOL in liquid crystal MBBA aligned by magnetic field (a) and radical Rb in liquid crystal 5CB aligned by magnetic field (b) and aligned by pores of SPPE (c). (Figure appears in color online.)

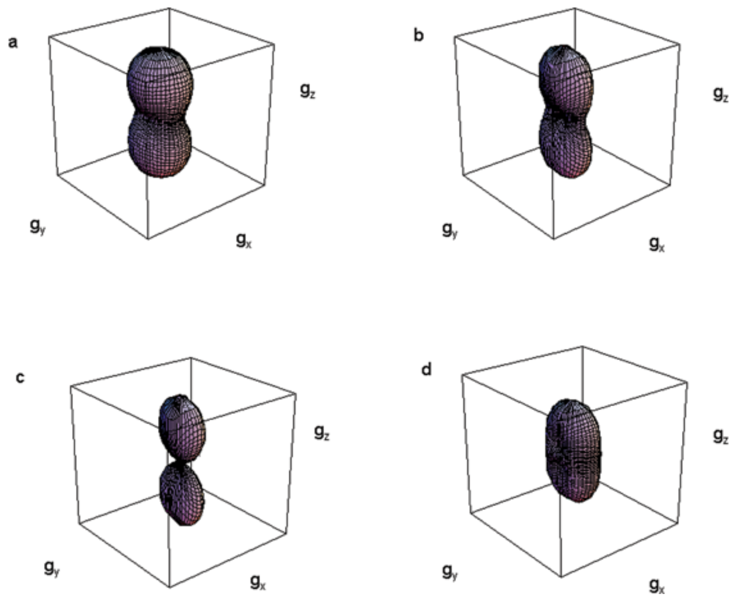

Figure 5. The orientation distribution functions of radicals Ra (a), Rb (b), Rc (c) and Rd (d) in five times stretched polyethylene. (Figure appears in color online.)

case of alignment by pores is considerably less then corresponding value in the case of alignment by magnetic field. Undoubtedly, smaller anisotropy of ODF in the case of SPPE is a result of less alignment of pores in polyethylene.

The ODFs of spin probes Ra, Rb, Rc in stretched HDPE are presented in Figure 5. The ODF for Ra is described by coefficients $j = 2$ in series (1) only, whereas for description of the ODF of Rc the coefficients with $j = 2$, 4 and 6 are necessary. From Figure 5 and Table 1 one can see that there is rather strong dependence of the order parameter on the length of alkyl substituent. Probably, alkyl substituents, which are similar to the polyethylene molecules, build into the matrix structure and define the spin probe order in the stretched polymer. For comparison the ODF of spin probes Rd (2-heptadecyl-2,2,3,4,5-pentamethylimidazoline-1-oxide, see Figure 1) in uniaxially stretched HDPE [15] is shown in Figure 5(d). Spin probe Rd carries one heptadecyl side chain. One can see that the novel spin probes reflect alignment of polymer more effectively than the spin probe Rd. It can be accounted for presence of two alkyl substituents attached to rigid nitroxide core in these spin probes. Indeed, two alkyl chains being embedded into polyethylene matrix define position of central nitroxide core more inflexibly than one chain.

4. Conclusion

The orientation distribution functions of the novel nitroxide radicals were determined in aligned liquid crystals and stretched polymers. The true order parameters were estimated for all systems under consideration. It was shown that these radicals can be effectively used for measurements of orientation alignment of both liquid crystals and polymers.

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