# Determination of orientation distribution function of anisotropic paramagnetic species by analysis of ESR spectra angular dependence

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## Abstract

A method has been developed to determine orientation distribution function (ODF) of anisotropic paramagnetic species by analysis of the angular dependence of the ESR spectra. The method is based on computational spectra simulation. The ODF is represented as an expansion in terms of orthonormal functions. The expansion coefficients are determined through minimization of discrepancies between simulated spectra and experimental ones. By means of the suggested method we have determined the orientation distribution functions for radical probe 2,2,6,6-tetramethyl-4-ol-piperidinooxyl in 4-*n*-amyl-4′-cyanobiphenyl aligned by magnetic field and 2-septadecyl-2,3,4,5,5-pentamethylimidazolidine in polyethylene stretched films. In each case, thermal evolution of the ODF has been investigated.
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## 1. Introduction

Properties of many materials such as stretched polymers, Lengmuir–Blodgett films, etc., are controlled by an orientational order of their molecules. The most precise characteristic of order is the orientation distribution function $\rho(\alpha, \beta, \gamma)$, that gives a number (or a proportion) of species oriented in an angular interval $\alpha + d\alpha$, $\beta + d\beta$, $\gamma + d\gamma$ ($\alpha, \beta, \gamma$ are Euler angles connecting a certain species coordinate system and the one of the sample). There are no methods at the present time that are intended for experimental determination of the ODF of partially oriented molecules. Partial order is usually characterized by the average values, e.g., orientation degree, order parameters, etc. [1–3]. This approach is valid when optical methods [2] or X-ray absorption spectroscopy [3] are used, since these methods inherently give the information, which is averaged over an ensemble of the species. The ESR method does not have this disadvantage. Resonance signal position for each species in an ESR spectrum depends on the species orientation in a magnetic field. Hence, ESR spectra can give more detailed information on the orientation distribution of molecules.

In several works [4–14] the ESR spectra were analysed to determine the orientation distribution of paramagnetic species. In the work [4], the ODF was determined by analysing the angular dependence of the parallel component of the spectrum. It has been assumed that the amplitude of this component is proportional to the number of species oriented parallel to the magnetic field. The works [5,6] show theoretically that the more molecules are aligned, the more calculated ODF will differ from the true ODF. It should be noted that these works [4–6] only deal with paramagnetic

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species that possess axially symmetric magnetic characteristics. The method discussed in [4–6] is not applicable in cases when the three principal values of g-tensor and/or hfs tensor differ. The other limitation of the method discussed in [4–6] consist in analysing several distinct points of the ESR spectrum only; therefore, a large amount of information about the orientation distribution of species contained in the whole spectrum is lost.

The whole ESR spectrum was analysed in [7–12], but determination of the paramagnetic species orientation distribution was made by the trial-and-error method. In that case, an assumption was made about the analytic expression of ODF and corresponding ESR spectra were simulated. The qualitative comparison of the simulated and the experimental spectra served as a guide for corroboration or refutation of the assumption made beforehand. The assumption was taken to be satisfactory when the positions and the proportions of intensities of the computed spectra components were in rough agreement with experiment.

The most precise method for determination of the orientation distribution of paramagnetic species was described in [13,14]. The orientation distribution in muscle fibres of myosin fragments labelled with nitroxide radicals was considered in these works. The distribution function was expressed as an expansion in terms of orthonormal functions. The expansion coefficients was picked in such a way that the theoretically computed ESR spectra agree with the experimental ones. It is noteworthy that the method proposed in [13,14] has been developed to fit the specific biological system and is not applicable in the general case. Besides, the question of the uniqueness of the solution obtained was not investigated.

In general, it is safe to say that there is no method at the present time to determine the ODF of paramagnetic species from the angular dependence of the ESR spectra, suitable for different systems. The aim of this work is to develop such a method.

## 2. Essentials of the method

We suggest the following method to determine the paramagnetic species ODF from the angular dependence of the ESR spectra. ESR spectra are recorded for several orientations of the sample in a magnetic field. For the same sample positions, the ESR spectra are simulated computationally, with the ODF represented as an expansion in terms of orthonormal functions with variable coefficients. The coefficients are determined by minimization of the discrepancy between the simulated and the experimental spectra. In this manner, the angular dependence of all the spectra points is analysed, and thus information contained in the spectra is used more fully.

The representation of the ODF should be different depending on the order of the system and the symmetry of paramagnetic centres. When axially anisotropic paramagnetic species form an axially symmetric sample, the orientation of each species in the sample is uniquely determined by the angle between the anisotropy axis of this species and the symmetry axis of the sample. In this case, the ODF is the function of only one angle. When axially anisotropic paramagnetic species are arbitrarily distributed in the sample, the orientation of each species is determined by the two angles that characterize the orientation of the anisotropy axis of this species in the reference frame associated with the sample. In this case the ODF is a function of the two angles. In an axially symmetric sample, the distribution function of species that have three different g-tensor and/or hfs-tensor principal values is also a function of the two angles. These angles characterize the orientation of the symmetry axis of the sample in the reference frame associated with a paramagnetic species.

It is known that a function that depends on two angles can be expressed in terms of spherical harmonics as follows:

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

where $P_j$ are Legendre polynomials, $P_j^k$ are associated Legendre functions.

For partially ordered systems with axial symmetry, an often used in the literature characteristic is the orientation factor of any molecular axis [15] $F = \frac{1}{2}(\langle 3\cos^2\theta \rangle -1)$, where $\theta$ is the angle of deflection of a molecule axis from the anisotropy axis of the sample, and angle brackets mean averaging over all the molecules. It is easy to show that the orientation factor of any molecular axis may be calculated from the expansion coefficients of the molecular distribution function by the following expressions: $F_x = -a_{20}/10 - 6a_{22}/5$, $F_y = -a_{20}/10 + 6a_{22}/5$, and $F_z = a_{20}/5$.

## 3. Uniqueness of determination of the orientation distribution function from ESR spectra

The distribution function that is determined from the analysis of ESR spectra is always symmetric vs. the origin of coordinates because effective parameters of a paramagnetic species do not change with reversing the magnetic field direction. Hence, a part of information about species orientation is inevitably lost. The symmetry of the ODF imposes certain limitations on its expansion coefficients. In particular, if the function is represented as a series of spherical harmonics, all $a_{jk}$ and $b_{jk}$ coefficients with an odd $j$ are equal to zero.

It is impossible to determine ODF of the paramagnetic species in a sample by analysing a single ESR spectrum, since the positions of resonance signals for species oriented differently with respect to magnetic field direction may coincide. It is necessary to analyse simultaneously several spectra recorded at different orientations of the sample in the magnetic field. Below we determine what sample orientations should be used when recording ESR spectra to uniquely define the ODF of the paramagnetic species through the simultaneous analysis of these spectra.

Let us assign the coordinate systems for the sample $(XYZ)$ and for a separate paramagnetic species $(xyz)$ arbitrarily. Let us put the sample into resonator of spectrometer so that the $Z$ axis is perpendicular to the magnetic field direction and record ESR spectrum. After that, the sample is turned by a certain angle about $Z$ axis and ESR spectrum is recorded again. Having done this procedure several times, we obtain a set of ESR spectra recorded with the sample rotation around its $Z$ axis. The magnetic field vector lies in the plane $(XY)$ of the sample reference frame during recording of all these spectra. Still, this set does not specify ODF uniquely since the positions of the paramagnetic species with respect to $(XY)$ plane cannot be discriminated. The set of ESR spectra recorded upon the sample rotation along a single axis defines an infinite family of ODFs, which vary continuously from true ODF to its mirror image in an orthogonal plane. This ambiguity will be named the "mirror problem." It is important to note that it allows to fix the orientational angles of a species reference frame $(xyz)$ with respect to $Z$ axis, whereas the unambiguous determination of ODF requires the knowledge of orientational angles with respect to $X$ and $Y$ axes as well. Therefore, to eliminate the ambiguity in the determination of the orientation distribution of species, ESR spectra should be recorded by rotating the sample around all three mutually orthogonal axes.

The consideration above can be illustrated by the example of the ODF of axially anisotropic paramagnetic species in a sample of arbitrary symmetry. Let us represent the true distribution function in the sample coordinate system as an expansion in terms of spherical harmonics (1) to the fourth order with coefficients $\{a_{jk}\}$, $\{b_{jk}\}$

$$\rho(\beta,\gamma) = 1/2a_{00} + 1/2a_{20}P_{20}(\cos\beta) + 1/2a_{40}P_{40}(\cos\beta)$$
$$+ P_{21}(\cos\beta)(a_{21}\cos(\gamma) + b_{21}\sin(\gamma))$$
$$+ P_{22}(\cos\beta)(a_{22}\cos(2\gamma) + b_{22}\sin(2\gamma))$$
$$+ P_{41}(\cos\beta)(a_{41}\cos(\gamma) + b_{41}\sin(\gamma))$$
$$+ P_{42}(\cos\beta)(a_{42}\cos(2\gamma) + b_{42}\sin(2\gamma))$$
$$+ P_{43}(\cos\beta)(a_{43}\cos(3\gamma) + b_{43}\sin(3\gamma))$$
$$+ P_{44}(\cos\beta)(a_{44}\cos(4\gamma) + b_{44}\sin(4\gamma)). \quad (2)$$

Let us reflect this function in the plane $(XY)$. The ESR spectra recorded with any direction of the magnetic field that lies in the plane $(YZ)$ will not change with this reflection. It is clear from Eq. (2) that the coefficients of the function reflected in the plane $(YZ)$ are related with those of the true function as: $a_{jk}^{\text{ref}} = a_{jk}$, $b_{jk}^{\text{ref}} = -b_{jk}$. Hence, $\{a_{jk}\}$ coefficients can be uniquely determined from the analysis of the ESR spectra recorded with the magnetic field direction rotated in the $(YZ)$ plane. It can be also shown that $b_{jk}$-coefficients cannot be unambiguously determined from the analysis of ESR spectra recorded with the rotating of magnetic field direction in $(YZ)$ plane; each of them may vary in the range from $-b_{jk}$ to $b_{jk}$ with no change of the spectra.

Let us consider now the sample coordinate systems $(X'Y'Z')$ and $(X''Y''Z'')$. The transitions $(XYZ) \to (X'Y'Z')$ and $(X'Y'Z') \to (X''Y''Z'')$ are performed by cyclic permutation of the coordinate axes. Let us denote the expansion coefficients of the true distribution function: in the $(X'Y'Z')$ coordinate system as $\{a'_{jk}\}$, $\{b'_{jk}\}$, and in the $(X''Y''Z'')$ coordinate system as $\{a''_{jk}\}$, $\{b''_{jk}\}$. As shown above, from ESR spectra recorded with the magnetic field direction rotated in the $(YZ)$ plane we can uniquely determine $\{a_{jk}\}$ coefficients, but not $\{b_{jk}\}$ coefficients. From the spectra recorded with the similar rotation of magnetic field direction in the $(Y'Z')$ plane, which is perpendicular to $(YZ)$, we can uniquely determine $\{a'_{jk}\}$ coefficients, and from the spectra recorded with the magnetic field direction lied in the $(Y''Z'')$ plane, which is perpendicular to both $(YZ)$ and $(Y'Z')$, we can uniquely determine $\{a''_{jk}\}$ coefficients. It is known that the coefficients of the function expansions into series of spherical harmonics in different coordinate systems are connected with each other by certain relationships. In our case, $b_{21} = a'_{21}$, $b_{22} = -a'_{21}/2$, $b_{41} = 21a'_{43}/2 - 3a'_{41}/4$, $b_{42} = a''_{41}/12 + 21a''_{43}/6$, $b_{43} = -3a'_{41}/72 - 3a'_{43}/4$, and $b_{44} = -a''_{41}/48 + a''_{43}/8$. Therefore, by means of recording ESR spectra with the sample rotation around three mutually orthogonal axes, one can uniquely determine all the expansion coefficients of the true distribution function.

The analysis of angular dependence of each point of an ESR spectrum actually implies solving of a system of linear equations relative to the expansion coefficients of the distribution function sought-for. We assumed on this basis that the number of experimental spectra necessary to uniquely determine the ODF should not exceed the number of unknown coefficients. This assumption has been confirmed during further computational testing of the method. Therefore, to determine all the second-order coefficients it is necessary to record five ESR spectra (note that the coefficient $a_{00}$ is proportional to the overall number of species and equals to 1 for a normalized distribution function). It can be shown that for any three of these five ESR spectra the magnetic field direction in the sample frame should be in one plane (denoted

P) that is chosen arbitrarily. The other two spectra should be recorded so, that the magnetic field direction resides in two planes that are orthogonal to P. To determine the fourth-order coefficients, one has to analyse nine ESR spectra at once. Five of these spectra should be recorded with the magnetic field vector lying in the plane P. The four remaining spectra should be recorded so that the magnetic field resides in two planes that are perpendicular to P (two spectra per each plane). Since the second-order and the fourth-order coefficients are determined independently, all the second-order and the fourth-order coefficients can be uniquely determined from nine spectra. To determine sixth-order coefficients one has to analyse 13 spectra at once, etc.

In some cases, the number of experimental spectra necessary for unambiguous determination of the ODF may be less than mentioned above. For example, when ESR spectra are recorded with a magnetic field vector in the sample plane that is the symmetry plane of the ODF the "mirror problem" does not exist, and $\{b_{jk}\}$ coefficients are equal to zero. In this case, for unique determination of all the second-order coefficients it is enough to record three spectra; five ESR spectra are sufficient for the fourth-order coefficients. If the distribution function describes the position of the symmetry axis of the sample in a reference frame of a paramagnetic species with coinciding principal axes of g-and hfs-tensors then the required number of ESR spectra will become even less. In this case ODF possesses $D_{2h}$ (mmm) symmetry since the effective magnetic resonance parameters are determined by the square of the direction cosines for magnetic field vector. Therefore, $a_{jk}$ in the series of spherical harmonics will only be non-zero with even $j$ and $k$. In this case, to determine the expansion coefficients up to the second order, one has to record two ESR spectra; determination of the fourth-order coefficients requires the concurrent analysis of three spectra; and four ESR spectra are sufficient to determine the sixth-order coefficients.

## 4. Details on the software implementation of the method

The implementation of the method is based on a program that allows to simulate an ESR spectrum computationally, and a minimizer program [16]. On this base, we have developed the software that is able to simulate a set of ESR spectra for various orientations of the sample in a magnetic field and to determine the coefficients of the expansion in terms of orthonormal functions so that the discrepancies between the simulated and experimental spectra are minimal.

A numerical simulation of ESR spectra in our program is carried out with the use of the spin Hamiltonian that includes second-order terms with regard to the energy of nuclear Zeeman interaction and contribution

of forbidden transitions. The program allows to simulate the ESR spectra of paramagnetic species with the anisotropic g-factor and anisotropic hyperfine structure. The principal axes of g- and hfs-tensors do not generally coincide and their relative orientation is given by Euler angles. A convolution of Gaussian and Lorentzian functions, as the most general representation of individual line shapes, is used for simulation. The program allows to take into account the dependence of a line shape on the orientation of the species in magnetic field that reflects line broadening as a result of an unresolved anisotropic hyperfine interaction. The line shape is given by a tensor, principal axes of which in a general case do not coincide with principal axes of the g-tensor. The ESR spectra may be calculated both in a rigid limit and with regard to librations of paramagnetic species in the cells of the matrix.

A minimiser program minimises the sum of squared deviations of the numerically simulated ESR spectra from the experimental spectra by means of varying the expansion coefficients of the distribution function. The global minimum is obtained with the non-linear least-squares method, a computational implementation of which is described in [21]. It maintains a secant approximation $S$ to second-order part of the least-squares Hessian and adaptively decides when to use this approximation. $S$ is "sized" before updating something that is similar to Oren–Luenberger scaling. The step choice algorithm is based on minimising a local quadratic model of the sum of squares function constrained to an elliptical trust region centred at the current approximate minimiser. When at some values of coefficients the distribution function has a region of negative values, a function that grows exponentially with growth of the absolute value of distribution function is added to each element of the deviations vector.

To simulate ESR spectra numerically one needs to know magnetic resonance parameters of species (i.e., g- and hfs-tensor components) as well as the shape and half-width of individual line. It is known that the mentioned parameters depend to some extent on the dielectric constant and complexability of the medium [1,17]. In this connection, it is desirable to preliminarily determine magnetic parameters of the probes used in the studied systems, as well as parameters that describe the line shape, from the experimental ESR spectrum of isotropic sample of the same composition. However, testing has shown that the scatter of experimentally determined hfs- and g-tensor components in the case of nitroxide radicals has no significant effect on determination of the orientation distribution function; the function retains its symmetry and orientation in the sample frame. Hence, in many cases it is possible to use the literature magnetic resonance parameters of the probes for ODF determination.

It is essential to note that simulation of isotropic spectrum allows choosing a suitable approximation for

calculation of spectra of experimental system under consideration. In particular, the assumption of coincidence of the *g*- and *hfs*-axes, neglect of nuclear Zeeman interaction and/or weak field approximation (effective magnetic field of electron on nucleus is greater then outside magnetic field) can be used for simplification of calculations. Quantitative comparison of experimental and calculated isotropic spectra is a test of validity of chosen simulation method.

## 5. Computational testing of the method

Series of computer experiments described below have been performed to test the validity of the suggested method and operability of the developed software.

ESR spectra corresponding to different sample orientations were calculated numerically for postulated orientation distribution function $\rho_i$. Then the $\rho_f$ was determined from the obtained set of spectra and compared with the original ODF. The disagreement between $\rho_f$ and $\rho_i$ was characterized by the following value:

$$\Delta = \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} |\rho_i - \rho_f| \mathrm{d}\alpha\, \mathrm{d}\beta\, \mathrm{d}\gamma. \qquad (3)$$

These numerical experiments were carried out for orientation distribution functions of various symmetry and for paramagnetic species with various anisotropy of magnetic properties. To illustrate this let us consider two distribution functions that significantly differ in symmetry. $\rho_1$ function (Fig. 1A) has three planes of symmetry. Expansion of this function in terms of spherical harmonics contains second-order members only. $\rho_2$ function (Fig. 1B) has no elements of symmetry. The expansion of $\rho_2$ into spherical harmonics contains non-zero fourth-order members. We have calculated the ESR spectra of the samples in which axially anisotropic paramagnetic species are distributed according to $\rho_1$ and $\rho_2$ functions. The orientation of the magnetic field in the sample frame in each case will be characterized by two Euler angles. In the case of $\rho_1$ function we calculated five spectra: (0°, 0°), (30°, 0°), (90°, 0°), (90°, 30°), and (60°, 90°). In the case of $\rho_2$ we calculated nine spectra: (0°, 0°), (30°, 0°), (45°, 0°), (60°, 0°), (90°, 0°), (90°, 30°), (90°, 60°), (90°, 90°), and (60°, 90°). Some of these spectra showing the angular dependence are given in Fig. 2. The following magnetic parameters were used for simulation: $g_x = g_y = 2.1000$, $g_z = 2.0900$, line half-width $\Delta H = 5$ G.

The orientation distribution functions determined through the analysis of the simulated spectra according to our method fully coincide with the original $\rho_1$ and $\rho_2$, which proves the validity of the method.

To elucidate the effect which random errors of ESR spectra recording have on determination of the ODF, we deliberately added a noise of various intensity to the simulated spectra. The orientation distribution functions
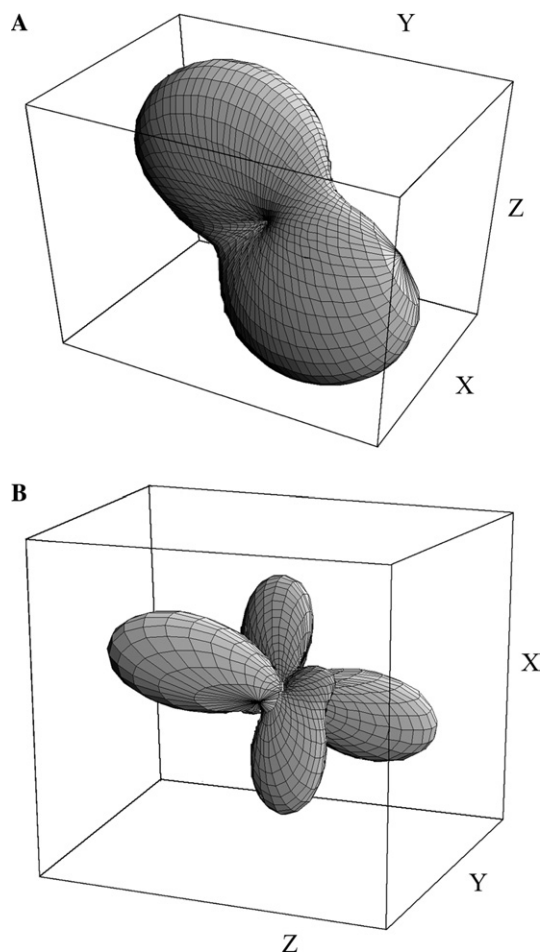


Fig. 1. Orientation distribution functions $\rho_1$ (A) has three planes of symmetry. Expansion of this function in terms of spherical harmonics contains second-order members only. Function $\rho_2$ (B) has no elements of symmetry. The expansion of $\rho_2$ into spherical harmonics contains non-zero fourth-order members.

determined from these "noisy" spectra are close to the original ones. The discrepancies of the functions from $\rho_1$ and $\rho_2$, calculated according to Eq. (3) are presented in Table 1. It is clear that the deviation of the distribution function determined from the spectra corresponding the true function $\rho_1$ does not exceed 5% given that the signal-to-noise ratio is greater than 3. In the case of orientation distribution $\rho_2$ that has more complex shape, random errors make a greater effect. $\rho_2$ determined from noisy spectra differs from the true one by 5% given that the signal-to-noise ratio is greater than 5.

Fig. 2 and Table 1 illustrate the following obvious conclusions:

- the ODF is reliably determined if the difference between distinct spectra of analysed set is more than experimental errors of spectra recording;
- the more subtle are the details of the ODF one needs to determine, the higher are the requirements to the spectra recording precision.
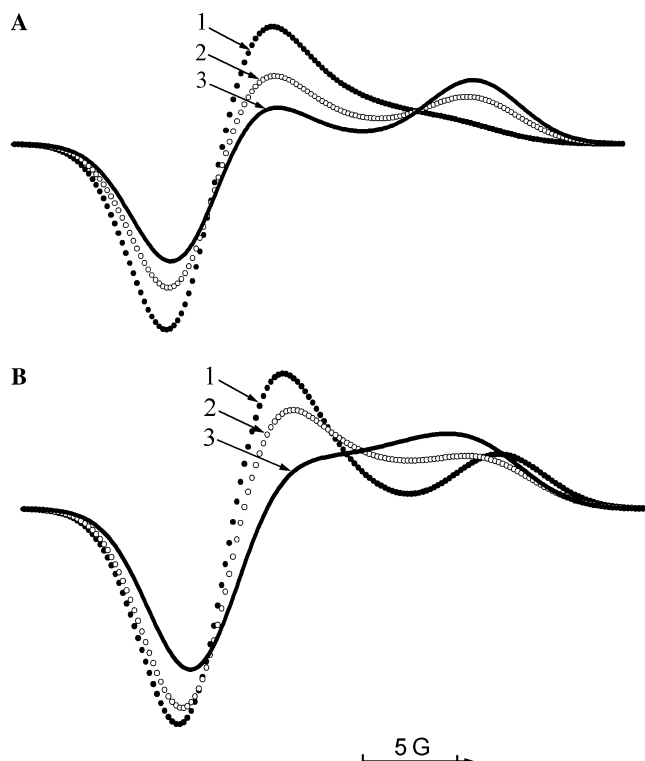
Fig. 2. Numerically calculated ESR spectra of the samples in which axially anisotropic paramagnetic species are distributed according to $\rho_1$ (A) and $\rho_2$ (B) functions. The spectra correspond to directions of magnetic field vector given by Euler angles $\beta$ and $\gamma$ in the sample frame. (A)—(1) $\beta = 60°$, $\gamma = 90°$; (2) $\beta = 30°$, $\gamma = 0°$; (3) $\beta = 90°$, $\gamma = 30°$. (B)—(1) $\beta = 60°$, $\gamma = 90°$; (2) $\beta = 90°$, $\gamma = 0°$; (3) $\beta = 90°$, $\gamma = 30°$.

Table 1
The discrepancies of orientation distribution functions determined from "noisy" spectra from postulated functions $\rho_1$ and $\rho_2$, calculated from Eq. (3)

| Signal-to-noise ratio | $\Delta$ (%) | |
|---|---|---|
| | For $\rho_1$ | For $\rho_2$ |
| 10 | 1,3 | 1,3 |
| 7 | 1,9 | 1,8 |
| 5 | 4,2 | 4,1 |
| 4 | 3,0 | 6,5 |
| 3 | 5,2 | 9,9 |
| 2 | 7,6 | 12,7 |
| 3/2 | 9,2 | — |

## 6. Testing of the method on experimental systems

The suggested method has been tested on two experimental systems. In the first case, we have studied the species orientation distribution of the 2,2,6,6-tetramethyl-4-ol-piperidinooxyl (TEMPOL) in a liquid crystal aligned by a magnetic field. 4-n-amyl-4'-cyanobiphenyl (5CB) was used as a matrix. It forms a nematic phase within the temperature range 22–35 °C [18]. In the second case, we have studied the orientation of the 2-septadecyl-2,3,4,5,5-pentamethylimidazolidine (further referred to as substituted imidazolidine) stable radical, in stretched polyethylene.

In Fig. 3A there are the ESR spectra of TEMPOL in glassy (−198 °C) aligned medium of 4-n-amyl-4'-cyanobiphenyl recorded at various sample orientations relative to the magnetic field direction. The angular dependence of the spectra indicates the ordering of paramagnetic species in the sample. Clearly, the aligned 4-n-amyl-4'-cyanobiphenyl matrix aligns TEMPOL molecules partially.

In Figs. 4A and B there are the ESR spectra of substituted imidazolidine in 5- and 11-times stretched polyethylene, recorded with various orientations of the sample in the magnetic field. It can be seen from the Fig. 4 that molecules of the probe partially align along with macromolecules of polyethylene with stretching the sample.

The samples in both experiments were axially symmetric. The axis of symmetry of a liquid crystal coincides with aligning magnetic field direction. The axis of symmetry of a polymer coincides with the stretching direction. As already noted above, the ODF of paramagnetic species that have three different principal values of the g-tensor in an axially symmetric sample will depend on two angles: $\beta$ and $\gamma$. These angles describe the orientation of the sample axis of symmetry in the reference frame, connected with a paramagnetic species. It should also be noted that when recording the angular dependence of the ESR spectra in our experiments, the magnetic field direction was rotated in a plane that includes the sample axis of symmetry. As has been noted above, in this case, in order to determine uniquely the
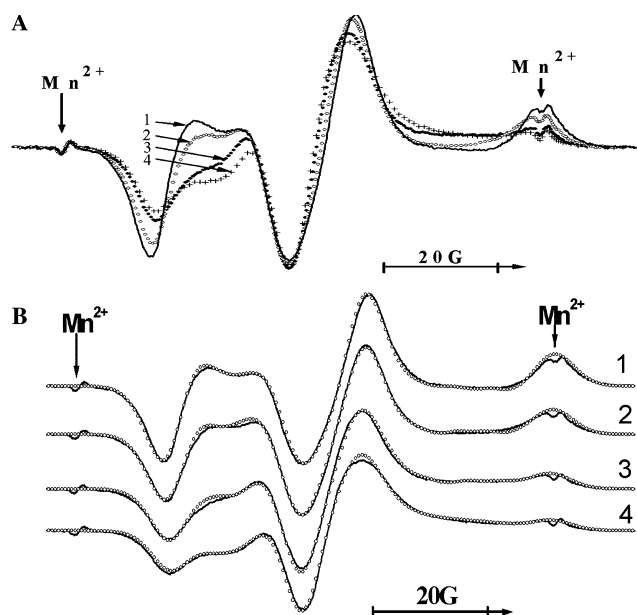


Fig. 3. The ESR spectra of TEMPOL in glassy (−196 °C) aligned 4-n-amyl-4'-cyanobiphenyl, recorded at various angles between the sample axis of symmetry and the magnetic field vector (1, 88°; 2, 58°; 3, 28°; and 4, −2°) (A). The simulation results for these spectra (B).
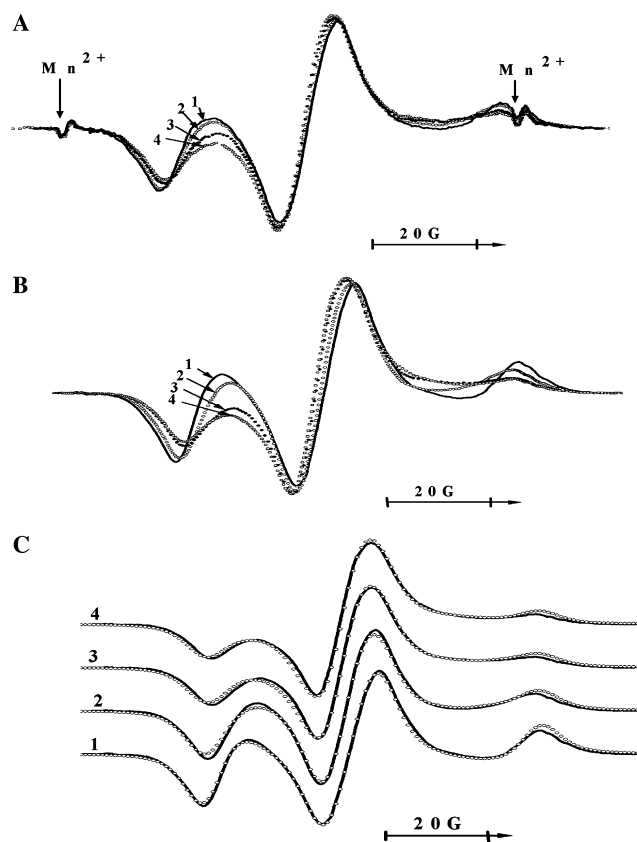
Fig. 4. The ESR spectra of substituted imidazolidine in stretched polyethylene recorded at various angles between the sample axis of symmetry and the magnetic field vector: (A) 5-times stretched sample (1, 3°; 2, 33°; 3, 123°; 4, 93°), (B) 11-times stretched sample (1, 10°; 2, 40°; 3, 70°; 4, 100°). The simulation results for the spectra in 11-times stretched sample in the same orientations (C).

expansion of the distribution function into spherical harmonics up to sixth order it is enough to record four ESR spectra.

In our experiments we have recorded six ESR spectra that correspond to different positions of the sample in magnetic field. Each analysed experimental spectrum was normalized by a value of its double integral. Note that angle between the sample axis of symmetry and the magnetic field vector in starting position ($\varphi$) is known approximately in our experiments as a result of errors in placing the sample in ampoule and ampoule in resonator of spectrometer. Precise value of $\varphi$ was found in the course of

simulation of spectra. In this process the angle $\varphi$ was taken as varied parameter together the expansion coefficients of the distribution functions. Practice has showed that accuracy of this method is ~0.5°.

The simulation results for some spectra of TEMPOL radical in 4-*n*-amyl-4′-cyanobiphenyl are given in Fig. 3B; analogous results for substituted imidazolidine in polyethylene are given in Fig. 4C. When calculating spectra, the distribution function has been represented as a series of spherical harmonics that includes second-order and fourth-order terms. Since in the case of nitroxide radicals principal axes of *g*- and *hfs*-tensors nearly coincide, just five expansion coefficients differ from zero: these are $a_{20}$, $a_{40}$, $a_{22}$, $a_{42}$, and $a_{44}$. In all of the experiments, inclusion of sixth-order terms into the series of spherical harmonics does not bring changes in a difference between calculated and experimental spectra, and the errors of sixth-order coefficients determination are larger than their absolute values. This result indicates that the details of the distribution function described by sixth-order terms cannot be determined from the experimental data presented.

Obtained coefficients of the expansion of the distribution functions of TEMPOL in aligned 4-*n*-amyl-4′-cyanobiphenyl and of substituted imidazolidine in 5- and 11-times stretched polyethylene are presented in Table 2. It can be seen that the absolute values of the coefficients describe the degree of order in the system, while their signs are connected with the orientation of the sample axis of anisotropy relative to the coordinate axes of paramagnetic species. For example, coefficient $a_{20}$ is proportional to the orientation factor of $Z$ axes of the probe molecules. $a_{20} < 0$ for TEMPOL in 4-*n*-amyl-4′-cyanobiphenyl, this implies mostly orthogonal orientation of $Z$ axes of TEMPOL molecules relative to the sample axis of anisotropy (the liquid crystal director). For substituted imidazolidine in polyethylene $a_{20} > 0$, and this means that $Z$ axes of imidazolidine molecules are aligned mostly in parallel with the sample axis of anisotropy (i.e., the direction of the polymer stretching).

When estimating errors of the evaluation of the expansion coefficients, we based our approach on the methodology from the work [19] devoted to the non-linear least-squares method applied for ESR spectra simulation. The errors were evaluated by means of two

Table 2
Coefficients of the expansion of the distribution functions of TEMPOL in aligned 4-*n*-amyl-4′-cyanobiphenyl and of substituted imidazolidine in 5- and 11-times stretched polyethylene

| | TEMPOL in aligned 4-*n*-amyl-4′-cyanobiphenyl | Substituted imidazolidine in 5-times stretched polyethylene | Substituted imidazolidine in 11-times stretched polyethylene |
|---|---|---|---|
| $a_{20}$ | $-0.872 \pm 0.007$ | $0.488 \pm 0.019$ | $0.878 \pm 0.070$ |
| $a_{22}$ | $0.082 \pm 0.004$ | $0.056 \pm 0.008$ | $0.095 \pm 0.018$ |
| $a_{40}$ | $0.247 \pm 0.015$ | $0.216 \pm 0.030$ | $0.673 \pm 0.128$ |
| $a_{42}$ | $-0.0004 \pm 0.0012$ | $0.010 \pm 0.003$ | $0.025 \pm 0.008$ |
| $a_{44}$ | $-0.0047 \pm 0.0003$ | $0.0 \pm 0.002$ | $0.0 \pm 0.002$ |

methods: with $\chi^2$-distribution and with Student distribution. Both methods give the same values of errors in our case. In addition, we visually estimated discrepancies between the calculated spectra and the experimental ones for various values of the expansion coefficients. This estimation indicated that the values of statistically calculated errors were somewhat understated. Perhaps, this can be explained by a presence of a non-statistical error in our experiments that is concerned with errors in determination of the angle of the sample turn. It was found that the statistically calculated errors that correspond to the confidence probability of 99% are rather close to the estimated values obtained when comparing the spectra visually. The confidence intervals for the probability of 99% are given in Table 2.

### 6.1. Orientation distribution function of TEMPOL in aligned 4-n-amyl-4′-cyanobiphenyl

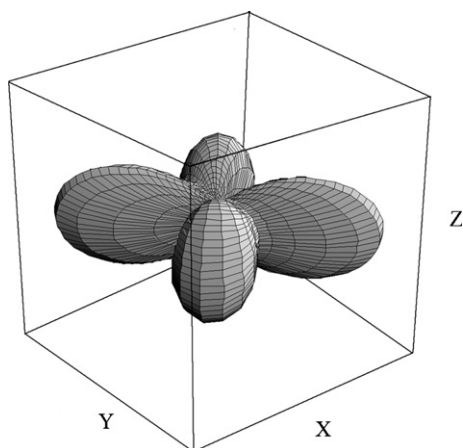The orientation distribution function of TEMPOL molecules in aligned 4-n-amyl-4′-cyanobiphenyl (5CB)



Fig. 5. The orientation distribution function of TEMPOL molecules in aligned 4-n-amyl-4′-cyanobiphenyl (−196 °C).
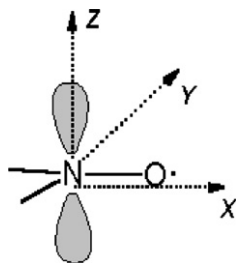


Fig. 6. The directions of the three principal g-tensor axes in molecules of nitroxide radicals.

constructed in accordance with the obtained expansion is shown in Fig. 5. This function demonstrates the orientation of the sample axis of anisotropy in a TEMPOL molecule reference frame. The three principal g-tensor axes were chosen as axes of coordinates; their directions in molecules of nitroxide radicals are shown in Fig. 6. From Fig. 5 one can see that Z axes of most TEMPOL molecules are directed orthogonally to the sample axis of anisotropy. Possibly it is a result of interaction of electron pairs of nitrogen and oxygen atoms with the π-system of the benzene ring of 4-n-amyl-4′-cyanobiphenyl. X and Y axes of majority of TEMPOL molecules are directed with the sample axis of anisotropy at angles of 50° and 40°, respectively. Hence, the analysis of ESR spectra angular dependence allows to determine the structure of the complex formed by TEMPOL and 4-n-amyl-4′-cyanobiphenyl.

The temperature evolution of the orientation distribution of TEMPOL in aligned 4-n-amyl-4′-cyanobiphenyl has been studied within the range from −196 to −6 °C. In Table 3, we have given orientation factors of Z axes of TEMPOL molecules that correspond to various annealing temperatures. As shown in Fig. 7, there are orientation distribution functions of TEMPOL in aligned 4-n-amyl-4′-cyanobiphenyl calculated for samples, annealed at temperatures of −78, −47, and −37 °C. It should be noted that all ODFs in Fig. 7 are represented to the same scale. From Table 3 and Fig. 7 it can be seen that in the temperature range from −196 to −47 °C a gradual off-orientation of TEMPOL molecules occurs in the sample. This, probably, reflects processes of relaxation of mechanical stresses and structural non-equilibrium in supercooled glass of 4-n-amyl-4′-cyanobiphenyl. In the range from −47 to −37 °C the orientation of paramagnetic probe sharply drops. It probably points on the existence of a phase transition of 4-n-amyl-4′-cyanobiphenyl in this temperature range. Indeed, the authors of the work [20] observed a phase transition of glassy 4-n-amyl-4′-cyanobiphenyl into crystal phase at −42 °C using calorimetric measurements.

### 6.2. The ODF of substituted imidazolidine in stretched polyethylene

The orientation distribution functions of molecules of substituted imidazolidine in stretched polyethylene obtained from ESR spectra are shown on Fig. 8. These functions display the orientation of the sample axis of anisotropy in an imidazolidine molecule frame. As in the previous case, we have used principal axes of the

Table 3
Orientation factors of Z axes of TEMPOL molecules in aligned 4-n-amyl-4′-cyanobiphenyl corresponding to various annealing temperatures

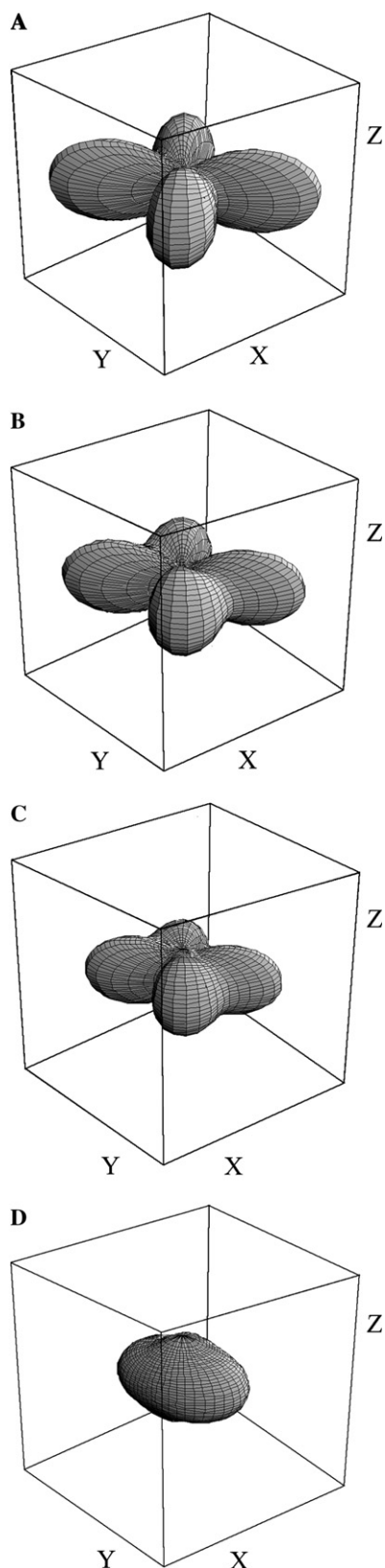| $T$ (°C) | −196 | −117 | −78 | −47 | −37 | −28 | −15 | −6 |
|---|---|---|---|---|---|---|---|---|
| $S_z \pm 0.003$ | −0.174 | −0.182 | −0.189 | −0.129 | −0.054 | −0.047 | −0.050 | −0.021 |

Fig. 7. The orientation distribution functions of TEMPOL in aligned 4-*n*-amyl-4′-cyanobiphenyl determined for unannealed sample (−196 °C) (A) and for samples annealed at temperatures of −78 °C (B), −47 °C (C), and −37 °C (D).


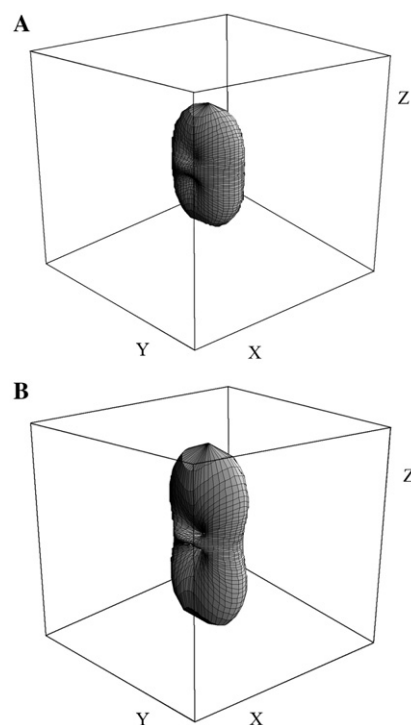
Fig. 8. The orientation distribution functions of substituted imidazolidine molecules in 5- (A) and 11-times (B) stretched polyethylene (−196 °C).

*g*-tensor as axes of coordinates. As expected, the order of the probe molecules grows with the polymer stretching degree.

It is clear from Fig. 8 that with stretching of polyethylene, the probe molecules align so that their *X* axes are directed mostly orthogonally to the sample axis of anisotropy. The alignment of *Y* and *Z* axes is significantly lower, although with the sample stretching the number of species grows that have their *Z* axes aligned with the sample axis of anisotropy. Hence, *X* axes of the probe in our experimental system are directed mostly orthogonally to stretched polyethylene macromolecules while *Z* axes are mostly parallel to them. According to the literature [17] the only possible complex of nitroxides with polyethylene is a π–σ complex. When forming such a complex, the *Z* axis of the imidazolidine molecule should be perpendicular to the polymer chain in contradiction with our experimental data. Therefore, experimental data indicate that the key factor is the geometrical property of a probe molecule having a long saturated fragment. Most likely septadecyl chain of imidazolidine aligns together with polyethylene macromolecules parallel with the direction of the sample stretching. In this case, the *X* axis of the probe will be roughly orthogonal to the sample axis of anisotropy and the *Z* axis will be roughly parallel to it, as shown on Fig. 9. In the context of this assumption, the greater alignment of *X* axes of the probe compared to *Y* and *Z* axes remains unexplained. To discussion of
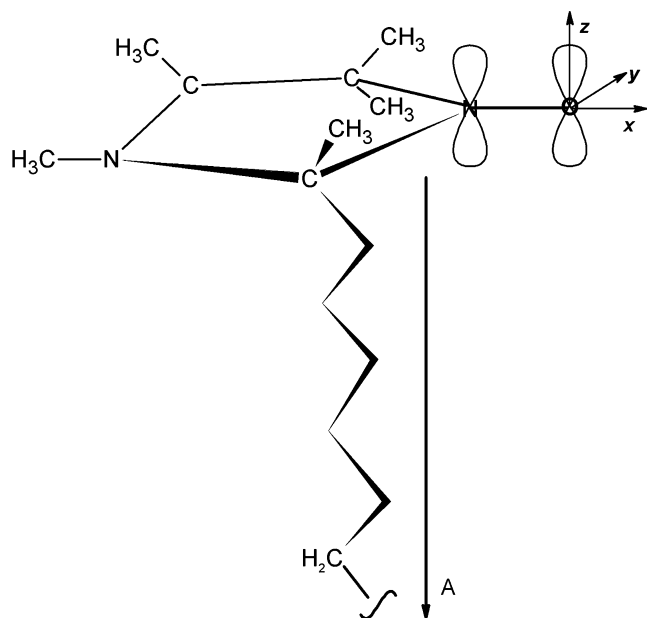
Fig. 9. A molecular structure of 2-septadecyl-2,3,4,5,5-pentamethy-limidazolidine.



Fig. 10. The orientation distribution functions of substituted imidaz-olidine molecules in polyethylene that was 11-times stretched and annealed subsequently at 52 °C (A), 81 °C (B), and 95 °C (C).

this question needs a more precise knowledge of the geometry of probe molecule and of its interaction with polyethylene.

Fig. 10 shows the orientation distribution functions of molecules of substituted imidazolidine in polyethylene that was 11-times stretched and annealed subsequently at 52, 81, and 95 °C (all ODFs are represented to the same scale). After each annealing, the sample was cooled to the temperature of −196 °C and the ODF was determined at this temperature. It is clear that with increase of the annealing temperature, the orientational order of the paramagnetic probe decreases significantly.

## 7. Conclusions

In general, we can conclude that the method suggested in this work to determine the ODF of anisotropic paramagnetic species from analysis of the angular dependence of ESR spectra is applicable to study partially oriented systems. The method is stable to the presence of errors in the spectra that are independent of sample orientation relative to a magnetic field; it is also sensitive enough to study the evolution of the orientation distribution of the probe during the relaxation of the matrix alignment. Unlike the methods that characterise the order of species with one averaged parameter, the ODF determination allows to study the mutual arrangement of admixture molecules and molecules of the medium. In present work, the method was applied for determination of ODF of nitroxide radicals but it is expected to be applicable to other spin system.
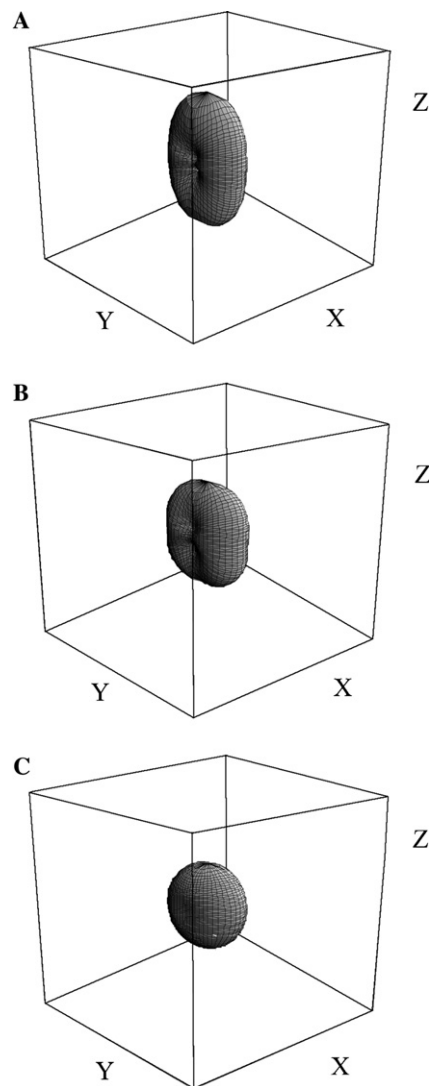
## 8. Experimental section

TEMPOL ("Sigma") and 4-*n*-amyl-4′-cyanobiphenyl ("Merk") were obtained commercially and were used without additional purification. Substituted imidazolidine synthesized by the procedure [22] was obtained from I.A. Grigoriev (Institute of Organic Chemistry, Novosibirsk Scientific Center). High-density polyethylene was obtained by extrusion ($M_w \sim 120{,}000$, degree of crystallinity 70%) and made up a film with a thickness of approximately 0.2 mm.

The stable radical was dissolved in the liquid crystal at 25 °C. The liquid crystal was put into a quartz ampoule that has inner diameter of 3 mm (the height of the sample was 10 mm) and aligned by a magnetic field of an ESR spectrometer (with the field strength of 3000 G) at a temperature of 25 °C. The liquid crystal

director was aligned perpendicular to the axis of the ampoule. The aligned sample was quickly cooled in the magnetic field to the temperature of $-196\,°C$. It was proved that experimental spectra do not change at this temperature at the time scale of experiment (i.e., several hours). Hence, orientation of the species is constant under the experimental conditions. Samples were annealed in a flow of gas nitrogen at a preset temperature. The precision of temperature control was $\pm 2\,°C$.

Substituted imidazolidine was put into polyethylene from a heptane solution; then the polymer was dried on air to constant weight. The samples of polyethylene containing the paramagnetic probe were stretched uniaxially at room temperature. During stretching, the length of the sample increased no more than 11 times. Further stretching was impossible, all attempts led to disruption of the sample. Fragments of the stretched films were put into quartz ampoules with inner diameter of 3 mm, with the stretching axis of the film directed perpendicularly to the ampoule axis. Samples were annealed in a water thermostat and an oil bath. The precision of temperature control was $\pm 2\,°C$.

The ESR spectra in all cases were recorded at $-196\,°C$ using a "Varian E-3" spectrometer. The ampoule with the sample was put in the spectrometer so that its axis was perpendicular to the magnetic field. The ESR spectra were recorded by consecutive turning of the ampoule around the axis with step $30°$ using a goniometer with accuracy $\pm 1°$.

Magnetic parameters of TEMPOL in 4-*n*-amyl-4′-cyanobiphenyl and of substituted imidazolidine in polyethylene, as well as parameters that describe the individual line shape were determined from the experimental ESR spectra of isotropic samples recorded at the temperature of $-196\,°C$. To accomplish this, the spectrum of the isotropic sample was simulated in each case and the parameters of interest were fitted so that the sum of squares of differences between the simulated and the experimental spectrum was minimal [21]. It was found that quality of simulation both spectrum of TEMPOL in 4-*n*-amyl-4′-cyanobiphenyl and spectrum of substituted imidazolidine in polyethylene is wholly satisfactory at weak field approximation.

The optimal magnetic parameters of TEMPOL in 4-*n*-amyl-4′-cyanobiphenyl were: $g_{xx} = 2.0096 \pm 0.0001$, $g_{yy} = 2.0067 \pm 0.0004$, and $g_{zz} = 2.0028 \pm 0.0001$; $a_{xx} = 8.4 \pm 0.4$ G, $a_{yy} = 3.6 \pm 1$ G, and $a_{zz} = 35.2 \pm 0.2$ G. The optimal magnetic parameters of substituted imidazolidine in polyethylene came to: $g_{xx} = 2.0084 \pm 0.0003$, $g_{yy} = 2.0074 \pm 0.0003$, and $g_{zz} = 2.0029 \pm 0.0001$; $a_{zz} = 32,5 \pm 0.3$ G, $a_{xx}$ and $a_{yy}$ less than 1.3 G. It should be noted that we were only interested in anisotropy of magnetic parameters of the probe; therefore, the average value of $g$ determined in our experiments is approximate.

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