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Determination of molecular orientation distribution of stable paramagnetic probes in stretched polymers

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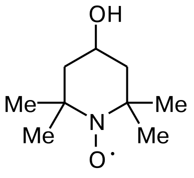
The possibility of determination of the orientation distribution functions of paramagnetic probes in stretched polymers by analyzing the angular dependence of EPR spectra was demonstrated taking two stable radicals, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl and 2-septadecyl-2,3,4,5,5-pentamethylimidazolidine, as examples. The method employed permits establishment of the preferred orientation of the probe molecules relative to the polymer macromolecules. The technique is responsive to changes in the orientation distribution of impurity particles on annealing of the matrix.

Key words: particle orientation distribution function; EPR spectroscopy; angular dependence of EPR spectra; simulation of EPR spectra; stretched polymers; polyethylene; polyamide-6; paramagnetic probe; 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL); 2,3,4,5,5-pentamethyl-2-septadecylimidazolidine.

Investigations of orientation ordering in polymers is of great interest, because this ordering is responsible for the anisotropy of microhardness, compressibility, optical, thermal, and many other properties of high-molecular-weight materials.[1] For instance, the tensile strength of polymers depends on the angle between the stretching force and the pre-stretching direction.[2] The most accurate characteristic of the orientation ordering of molecules is the orientation distribution function (ODF) $\rho(\alpha,\beta,\gamma)$, which shows the number (or proportion) of particles oriented in the interval of angles $\alpha + d\alpha$, $\beta + d\beta$, $\gamma + d\gamma$ (α, β, γ are the Euler angles relating the coordinate system of a certain particle to the coordinate system of the sample). Until recently, no methods suitable for experimental determination of the ODF were available. The orientation ordering of polymers was characterized by an averaged parameter, the orientation factor, which can be determined by various methods[3] including analysis of the angular dependence of EPR spectra.[4—6] This approach is quite natural when the orientation ordering of molecules is studied by the optical methods or X-ray absorption spectroscopy, because an intrinsic feature of these methods is to provide ensemble-averaged data. The EPR spectroscopy is free from this drawback. Position of the resonance signal of each particle in the EPR spectra depends on the particle orientation with respect to the magnetic field strength vector. Therefore, the EPR spectra can provide more detailed information on the orientation distribution of molecules.

Earlier,[7,8] we have developed a method for analyzing the angular dependence of EPR spectra, which allows not only the orientation factor of paramagnetic particles in the sample but also the ODF to be determined. The method involves recording a number of EPR spectra of an anisotropic sample at different orientations of the sample relative to the magnetic field strength vector. The EPR spectra corresponding to the experimental orientations of the sample in the magnetic field are simulated, the ODF being represented as an expansion in terms of orthonormal functions with variable coefficients. The expansion coefficients are determined by minimizing the sum of the squared deviations of the calculated spectra from the experimental ones using nonlinear least squares method.[9] This approach was evaluated taking a stable paramagnetic probe in an oriented liquid crystal as an example.[8] The aim of this work was to employ the method[7,8] for the determination of the ODF of paramagnetic probes in oriented polymer matrices.

The model objects were two polymers with strongly different deformability, namely, high-density polyethylene (HDPE) and poly(imino(1-oxohexamethylene)) (polyamide-6, PA6). The paramagnetic probes were 4-hydroxy-2,2,6,6-tetramethypiperidine-1-oxyl



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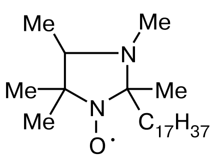

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(TEMPOL, **1**) and a substituted imidazolidine, 2,3,4,5,5-pentamethyl-2-septadecylimidazolidine (**2**).

Experimental

The HDPE and PA6 samples were films about 0.2 mm thick. TEMPOL is a commercially available reagent, which was used without additional purification. Compound **2** was synthesized following a known procedure[10] and kindly submitted by I. A. Grigor´ev (Institute of Organic Chemistry, Novosibirsk Scientific Center).

The substituted imidazolidine was introduced into the HDPE sample from a heptane solution and the polymer was dried in air until constant weight. The paramagnetic probe concentration in the polymer was ~$5 \cdot 10^{17}$ particle cm^{-3}. The HDPE samples containing the paramagnetic probe were uniaxially stretched at room temperature. The stretched samples were characterized by at most tenfold relative elongation because further stretching led to sample breaking. These results are consistent with the published data on cold drawing of HDPE.[11]

TEMPOL was introduced into the PA6 samples from a solution in EtOH and the polymer was also dried in air until constant weight. Here, the probe concentration in the polymer was ~$1 \cdot 10^{18}$ particle cm^{-3}. The PA6 samples containing paramagnetic probe were uniaxially stretched at 70 °C, because significant deformation of the polymer at room temperature is impossible. The stretched samples were characterized by about fourfold relative elongation.

Fragments of the stretched polymer films were placed into quartz tubes (internal diameter 3 mm), the stretching axes of the films being directed perpendicular to the tube axis. EPR spectra were recorded on a Varian E-3 EPR spectrometer at 77 K. A tube with a sample was placed in the spectrometer cavity in such a way that the tube axis be perpendicular to the direction of the magnetic field strength vector. The EPR spectra were recorded after successive turns of the tube about its axis with an increment of 30° and an accuracy of ±1°. The samples were annealed in a water thermostat and on an oil bath. The thermostatting accuracy was ±2 °C. Each annealing was followed by cooling the sample again down to 77 K and recording its EPR spectrum at this temperature.

Results and Discussion

Determination of the magnetic-resonance parameters of substituted imidazolidine in HDPE matrix and of TEMPOL in PA6 matrix. Analysis of the EPR spectra in order to extract information on the orientation ordering of paramagnetic particles requires knowledge of their magnetic-resonance parameters (components of the *g*-tensor and HFI tensor). It is known[12,13] that the magnetic-resonance parameters vary to some extent depending on the medium polarity and the ability of the medium to complexation. In this connection the magnetic parameters of the probes in the polymer matrices under study and the parameters describing the shape of individual lines were detected based on the experimental EPR spectra of isotropic (unstretched) samples recorded at 77 K. To this end, in each case the spectrum of the isotropic sample was theoretically simulated and the parameters were chosen in such a way that the sum of the squared deviations of the theoretically calculated spectrum from the experimental one be minimum.[14]

The magnetic parameters of TEMPOL in the HDPE matrix were as follows: $g_{xx} = 2.0096 \pm 0.0001$, $g_{yy} = 2.0065 \pm 0.0003$, $g_{zz} = 2.0020 \pm 0.0001$; $a_{xx} = 0.64 \pm 0.03$ mT, $a_{yy} = 0.53 \pm 0.03$ mT, and $a_{zz} = 3.48 \pm 0.03$ mT. These values coincide with the published data[15—17] within the limits of experimental error. The magnetic parameters of substituted imidazolidine in the PA6 matrix were $g_{xx} = 2.0084 \pm 0.0003$, $g_{yy} = 2.0074 \pm 0.0003$, $g_{zz} = 2.0029 \pm 0.0001$; $a_{zz} = 3.25 \pm 0.03$ mT, and a_{xx} and a_{yy} smaller than 0.13 mT. It should be noted that we interested only in the anisotropy of the magnetic parameters of the probe; therefore, the average *g* value in our experiments was determined very approximately. Unfortunately, the magnetic parameters of compound **2** have not been reported as yet. However, the values we have obtained are similar to the magnetic parameters of 2,2,3,4,5,5-sextamethylimidazolidine in methanol and toluene.[12]

For both probes the best description of the EPR spectra of isotropic samples was achieved when the individual lineshape was described by convolution of the Gaussian and Lorentz functions and the half-widths of both lines represented by tensor quantities. The directions of the principal axes of both tensors coincide with the directions of the principal axes of the *g*-tensor.

The orientation distribution function of compound 2 in stretched HDPE. The EPR spectra of probe **2** in the HDPE sample at four- and tenfold relative elongations are shown in Figs. 1, *a* and 1, *b* respectively. The spectra recorded at different orientations of the sample relative to the magnetic field strength vector differ from one another. This suggests partial orientation of the probe molecules along with the polyethylene molecules on stretching of the sample.

The experimental conditions described above make it possible to simplify the known technique.[7,8] In our experiments, polymer films were uniaxially stretched and, hence, the samples were axially symmetric. In this case the ODF of the paramagnetic particles characterized by three different principal values of the *g*-tensor and the HFI tensor depends on two angles (β and γ), which determine the orientation of the symmetry axis of the sample in the coordinate system related to the paramagnetic particle. Then, the ODF can be represented as an expansion in terms of spherical harmonics:

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

where P_j are the *j*th power Legendre polynomials, P_j^k are the *j*th power Legendre added functions of the first kind

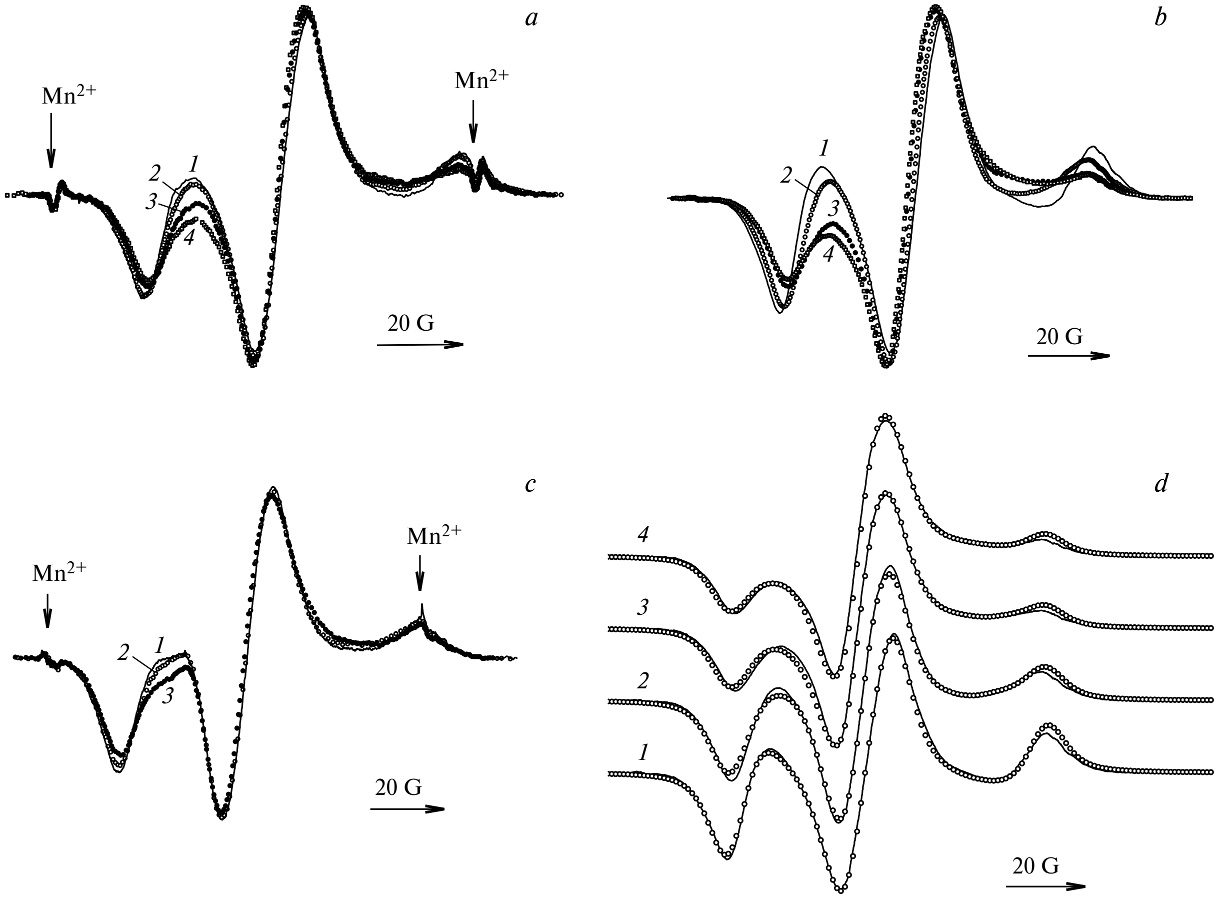

Fig. 1. EPR spectra recorded at different angles between the stretching axis of the sample and the magnetic field strength vector: *a* — substituted imidazolidine in polyethylene (fourfold relative elongation) (*1* — 3°, *2* — 33°, *3* — 123°, *4* — 93°); *b* — substituted imidazolidine in polyethylene (tenfold relative elongation) (*1* — 10°, *2* — 40°, *3* — 70°, *4* — 100°); *c* — TEMPOL in PA-6 (fourfold relative elongation) (*1* — 112°, *2* — 52°, *3* — −8°); *d* — results of simulation of the EPR spectra of substituted imidazolidine in polyethylene (tenfold relative elongation) (*1* — 10°, *2* — 40°, *3* — 70°, *4* — 100°); lines — experiment, circles — results of calculations.

and the kth order, and a_{jk} and b_{jk} are the expansion coefficients.

In the coordinate system related with the paramagnetic particle any ODF is a symmetric function because the effective magnetic-resonance parameters of the particle are determined by the squared direction cosines of the magnetic field strength vector in the same coordinate system. Because of this only the coefficients a_{jk} with even j and k in expansion (1) differ from zero.

In this work, in order to obtain the ODF expansion coefficients, we simultaneously simulated a total of six EPR spectra corresponding to different angles between the stretching axis of the sample and the magnetic field strength vector. The ODF was determined by simultaneous simulation of these spectra and search for a global minimum of the deviation of the simulated spectra from the experimental ones. It should be noted that in our experiments the angle φ between the stretching axis of the sample and the magnetic field strength vector at the initial sample position is known only approximately. This is due to uncertainties related to the setting of the polymer film in the tube and to the tube setting in the resonator of the spectrometer. The exact value of the angle φ is determined in the course of spectral simulation, the angle φ being treated as a variable parameter in addition to the ODF expansion coefficients. Our experience shows that in the course of minimization of the deviations of the simulated spectra from the experimental ones the angle φ is determined with a very small error of about 0.5°.

The minimization procedure showed that the spectra shown in Figs. 1, *a* and 1, *b* can be simulated using only the second and fourth order terms in expansion (1), because the inclusion of the sixth order terms does not improve the description of the experimental spectra. In this case a total of six expansion coefficients, namely, a_{00}, a_{20}, a_{40}, a_{22}, a_{42}, and a_{44} differ from zero. The a_{00} coefficient is proportional to the total number of particles; for the normaized ODF it is equal to unity. As an illustration, Fig. 1, *d* presents the results of simulation of certain EPR spectra of the stretched sample characterized by tenfold

Table 1. Coefficients of expansion of the orientation distribution functions of paramagnetic probes in oriented polymers in terms of spherical harmonics

Polymer	a_{20}	a_{22}	a_{40}	a_{42}	a_{44}
Substituted imidazolidine in polyethylene (fourfold relative elongation of the sample)	0.488±0.016	0.056±0.007	0.216±0.044	0.010±0.006	0.0017±0.0006
Substituted imidazolidine in polyethylene (tenfold relative elongation of the sample)	0.878±0.018	0.095±0.018	0.673±0.006	0.025±0.004	0.0±0.0006
TEMPOL in polyamide (fourfold relative elongation of the sample)	−0.186±0.019	0.037±0.009	—	—	—

relative elongation. The ODF expansion coefficients obtained by simulation of the EPR spectra of the stretched samples characterized by four- and tenfold relative elongation are listed in Table 1. (As can be seen, the expansion coefficients for the latter sample are much larger than those for the former.)

When estimating the errors in determination of the expansion coefficients, we were guided by the results of a study[18] concerned with the application of nonlinear least squares method to simulation of EPR spectra. The errors were calculated by two methods, with allowance for χ^2-distribution and taking into account the Student distribution. The covariation matrix was calculated using a minimization program.[9] In our case both methods gave the same errors. Besides, visual estimation of the deviations of the calculated spectra from the experimental ones at different values of the expansion coefficients showed that the calculated errors are somewhat underestimated. This can probably be due to a systematic error in our experiments, which was related to inexact determination of the angle of rotation of the sample. It was also established that the errors corresponding to a 99% confidence level are quite similar to the estimates obtained by visual comparison of the spectra. The confidence intervals at 99% probability are listed in Table 1.

The ODFs of molecules **2** in the HDPE sample (for both four- and tenfold relative elongations) constructed using the expansion coefficients obtained are shown in Fig. 2. These functions demonstrate position of the anisotropy axis of the sample in the coordinate system related to molecule **2** (principal axes of the *g*-tensor were used as the coordinate axes). As should be expected, the greater the stretching of the sample, the higher the ordering of the probe molecules.

Usually, the ordering of molecules in uniaxially stretched polymers is characterized by the orientation factor[2,3,19]

$$F = 0.5(\langle 3\cos^2\theta\rangle - 1),$$

where θ is the angle of deviation of a given axis of the molecule from the anisotropy axis of the sample and the angular brackets denote the averaging over all molecules. The orientation factor of each molecular axis can be calculated using the expansion coefficients of the ODF in terms of spherical harmonics. The orientation factors of the principal axes of the *g*-tensor of substituted imidazolidine in the HDPE sample (for both four- and tenfold relative elongations) are shown in Table 2.

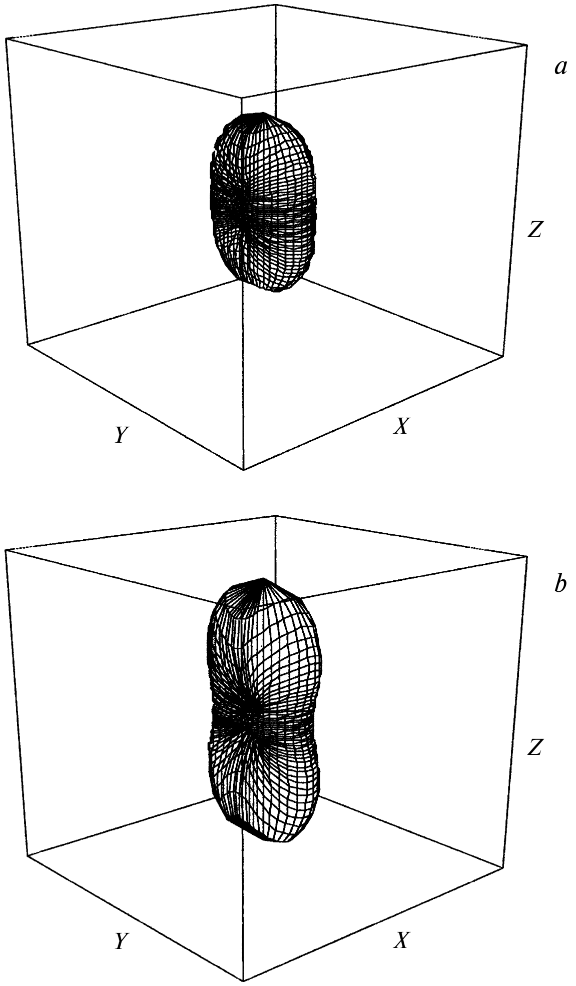

Fig. 2. Orientation distribution functions of substituted imidazolidine in stretched polyethylene films: fourfold (*a*) and tenfold (*b*) relative elongation of the sample.

Orientation distribution function of TEMPOL in polyamide-6. The angular dependence of the EPR spectra of stable radical TEMPOL in the stretched PA6 sample (four-

Table 2. Orientation factors of magnetic axes of paramagnetic probes in oriented polymers

Polymer	$-F_X$	F_Y	F_Z
Substituted imidazolidine in polyethylene (fourfold relative elongation of the sample)	0.116±0.009	0.018±0.009	0.098±0.003
Substituted imidazolidine in polyethylene (tenfold relative elongation of the sample)	0.202±0.022	0.026±0.022	0.176±0.004
TEMPOL in polyamide (fourfold relative elongation of the sample)	0.026±0.011	0.063±0.011	−0.037±0.004

fold relative elongation) is shown in Fig. 1, *c*. In this case the spectra recorded at different positions of the sample relative to the magnetic field strength vector differ insignificantly. The EPR spectra of this system were simulated using only the second order terms. An increase in the number of expansion coefficients does not improve the description of the experimental spectra. The expansion coefficients of the ODF in terms of spherical harmonics, obtained after simulation are listed in Table 1. The absolute values of these coefficients are much smaller than the corresponding coefficients for the HDPE—substituted imidazolidine system.

The orientation distribution function of TEMPOL molecules in the stretched PA6 sample constructed using the expansion coefficients obtained is shown in Fig. 3. As above, the principal axes of the *g*-tensor were chosen as the coordinate axes of the probe. The orientation factors of these axes of the TEMPOL molecules in the stretched polyamide-6 sample are listed in Table 2.

Evolution of the orientation ordering of paramagnetic probes in stretched polymers on annealing of polymer. The ODFs of molecules **2** in the HDPE sample (tenfold relative elongation) successively annealed at 325, 354, and 368 K are shown in Fig. 4.

Apparently, the evolution of the ODF indicates some relaxation processes which lead to a decrease in the orientation ordering of the polymer matrix. It should be noted that in this case the annealing temperature much exceeds the glass transition temperature of the polymer (T_g(polyethylene) = 148 K), being near its melting temperature (T_m(polyethylene) = 410.5 K).

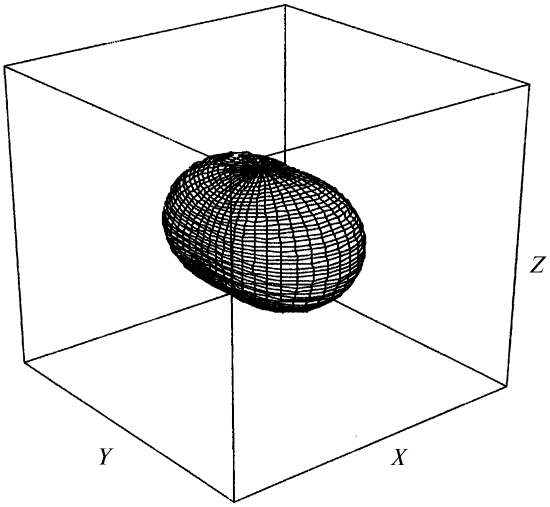

Fig. 3. Orientation distribution function of TEMPOL in stretched polyamide.

Stretched PA6 samples were annealed in the temperature interval 343—423 K. At temperatures above 423 K, the paramagnetic probe quickly loses. Changes in the ODF in this temperature range are comparable with the experimental errors.

Probably, this is due to the fact that here the annealing temperature is slightly higher than the glass transition temperature of the polymer (T_g(PA6) = 313—360 K), being appreciably different from its melting temperature (T_m(PA6) = 504 K).

Mutual position of paramagnetic probes and polymer matrix molecules. The ODFs of the probe molecules, obtained by analyzing the EPR spectra demonstrate a preferred orientation of these molecules relative to the direction of polymer stretching. However, since the polymer macromolecules are oriented along the sample stretching direction, these ODFs allow one to draw some conclusions about the relative arrangement of the probe molecules and the macromolecules of the polymer matrix.

Two reasons that can determine positions of probe molecules in orientationally ordered polymers have been discussed in the literature. First, if a paramagnetic particle has an extended shape, the long axis of the particle is aligned to the oriented macromolecules.[18] Second, one should take into account the possibility of complexation of paramagnetic molecules with polymer molecules. For instance, nitroxyl radicals can form complexes of different structure with many classes of compounds.[13]

Consider the ODF of substituted imidazolidine in stretched HDPE. When stretching the sample, the probe molecules are oriented in such a way that their *X* axes be mainly perpendicular to the anisotropy axis of the sample (see Fig. 2). The degree of orientation ordering of the *Y* and *Z* axes is much lower; however, an increase in the sample deformation leads to an increase in the number of particles whose *Z* axes are oriented along the anisotropy axis of the sample. Thus, in our experimental system the *X* axes of the probe molecules should mainly be directed perpendicular and the *Z* axes be directed parallel to the extended polyethylene macromolecules. It is known that in nitroxyl radicals the *X* axis is directed along the N—O bond and the *Z* axis along the π-orbital occupied by an unpaired electron and distributed nearly equally between the N and O atoms (Fig. 5). The only possible

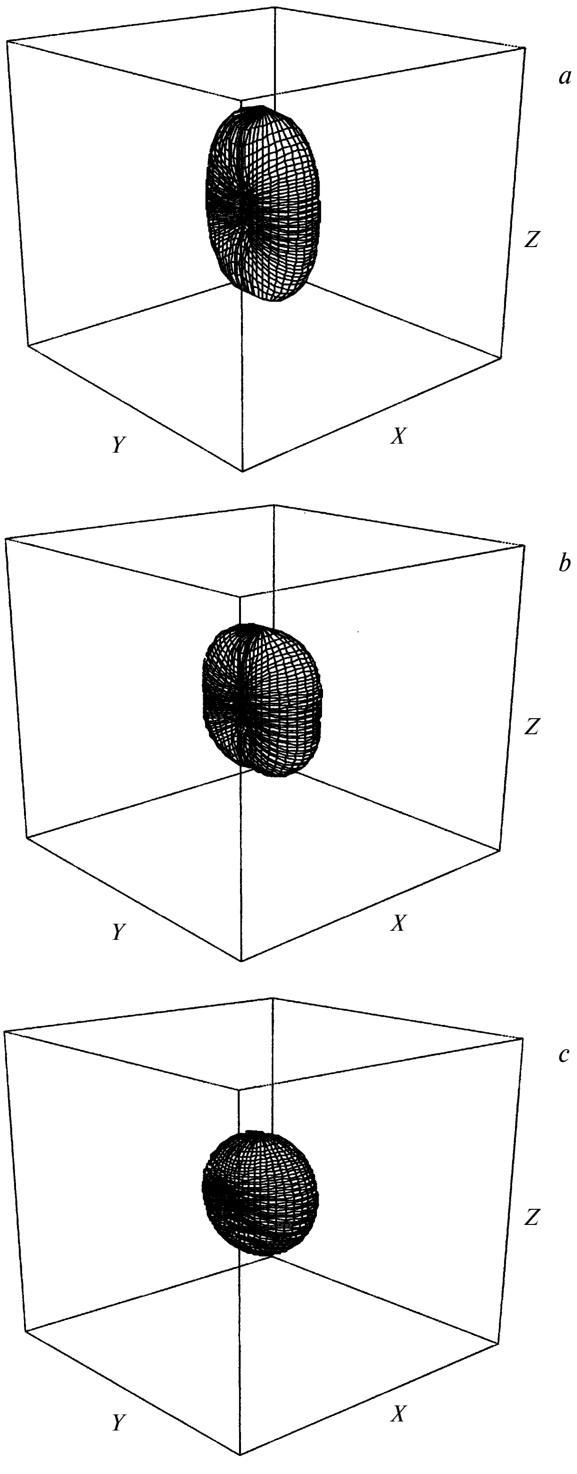

Fig. 4. Orientation distribution functions of substituted imidazolidine in polyethylene (tenfold relative elongation of the sample) successively annealed at 325 (*a*), 354 (*b*) and 368 K (*c*).

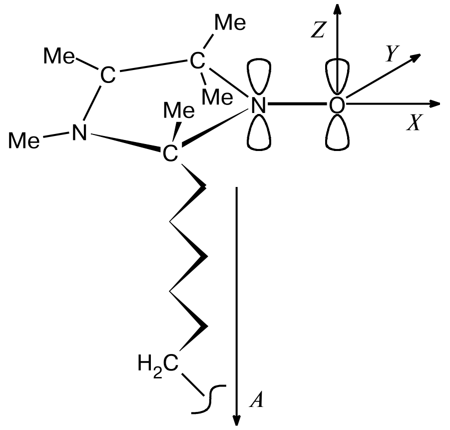

Fig. 5. The molecule of 2-septadecyl-2,3,4,5,5-pentamethylimidazolidine; *X*, *Y*, and *Z* are the principal axes of the *g*-tensor and *A* is the direction of polymer stretching.

complex of substituted imidazolidine with polyethylene is a π—σ-complex, which implies that the *Z* axis of molecule **2** is oriented perpendicular to the polymer chain, which contradicts our experimental data. Thus, in this case the probe orientation is governed by the presence of long alkyl substituent. Most probably, the septadecyl substituents in molecule **2** are aligned to the polyethylene macromolecules oriented along the stretching axis of the sample. In this case the *X* axis of the probe will be directed nearly perpendicular while the *Z* axis nearly parallel to the anisotropy axis of the sample (see Fig. 5). But the reason for higher orientation ordering of the *X* axes of the probes as compared to the *Y* and *Z* axes remains unclear and its establishment requires better knowledge of the geometry of the probe molecule and its interaction with the polyethyelene molecules.

Consider the values of the orientation factors for different axes of molecule **2**, calculated for both stretched samples (see Table 2). The negative value of the orientation factor of the *X* axis corresponds to perpendicular orientation of this axis relative to the direction of sample stretching (an ideal case is $F_X = -0.5$). The F_X values obtained in our experiments are much smaller than this value. This suggests that the paramagnetic fragments of the probe molecules are in the amorphoous phase of the polymer. Indeed, it is known[19—21] that in the crystalline phase of the stretched polymer the orientation factor of the macromolecules approaches unity (*cf.* 0.35—0.55 for the amorphous phase of stretched polyethylene[19]). In our experiments the degree of ordering of paramagnetic fragments also does not reach the maximum possible value. Thus, the paramagnetic fragments of the substituted imidazolidine are likely in the amorphous phase of HDPE.

Consider now the ODF of TEMPOL radical in stretched PA6 sample. In this case the probe molecules are oriented in such a fashion that their *Y* axes are mainly directed parallel while the *Z* and *X* axes are mainly directed perpendicular to the anisotropy axis of the sample (see Fig. 3). In contrast to the substituted imidazolidine molecules the TEMPOL molecules have no extended shape; therefore, in this case the main reason for mutual alignment with the PA6 molecules seems to be complex-

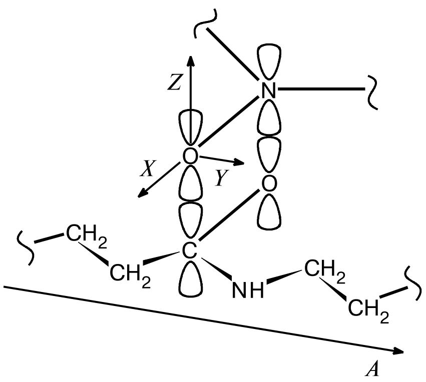

Fig. 6. Interaction of nitroxyl radical with stretched polyamide resulting in a π—π-complex; *X*, *Y*, and *Z* are the principal axes of the *g*-tensor and *A* is the direction of polymer stretching.

ation. Nitroxyl radicals can form π—π-, π—n- and n—π-complexes with polyamide molecules, the last two types being more stable in solutions.[13] However, our experimental results indicate the formation of a π—π-complex in the TEMPOL—PA6 system. Here, the electron cloud formed by the lone electron pairs of the N and O atoms of the TEMPOL molecule interacts with the electron cloud of the C—O π-bond of the polyamide-6 molecule and the *Z* and *X* axes of the probe are oriented perpendicular while the *Y* axis is oriented parallel to the direction of sample stretching (Fig. 6). The formation of π—n- or n—π-complexes must be characterized by another orientation of the axes of the TEMPOL molecules relative to the anisotropy axis of the sample. One can admit that π—π-complex is the most geometrically preferred structure in the oriented polymer.

As can be seen in Fig. 3 and Table 2, the degree of orientation ordering of the TEMPOL molecules in stretched PA6 is much lower than the degree of ordering of substituted imidazolidine in HDPE. Most probably, this is due to the low complexation energy of **2** with PA6 molecules.

The results obtained show that determination of the ODF of a paramagnetic impurity allows one to obtain new information both on the interaction of impurity molecules with the polymer matrix and on the changes in the polymer structure under the action of external factors (in this case, temperature).

Thus, the method[7,8] of determination of the spatial orientation of paramagnetic particles by analyzing the angular dependence of EPR spectra can be employed in studies on the ordering of polymeric materials. The method allows one to determine the probe ODF in systems with low degree of ordering, being sufficiently responsive for studying the evolution of the ODF. In contrast to the methods that characterize the degree of particle ordering by one averaged parameter, the determination of the ODF makes it possible to study the mutual position of the impurity and matrix molecules.

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