

Rotational mobility of guest molecules studied by method of oriented spin probe

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Oriented spin probe method was used for study of rotational mobility of di-*p*-anisyl nitroxide in low-temperature ethanol, toluene and isopropylbenzene glasses as well as in glassy polystyrene, poly(*N*-vinylpyrrolidone) and polyvinyl butyral matrixes. Alignment of probe molecules in initially isotropic samples was induced by polarized light irradiation (photoselection phenomenon). The temperature dependencies of relaxation of alignment were measured. The rotational relaxation of light-induced alignment in low-temperature glasses was found to complete near the glass transition temperature. A step-type relaxation of alignment on a time scale of minutes has been found in the temperature range 150–300 K for polystyrene, poly(*N*-vinylpyrrolidone) and polyvinyl butyral. The results are in dramatic contradiction with the commonly known rotational correlation times of probe molecules in glassy polymers obtained by the traditional spin probe method. The nonlinear least-squares fitting of experimental EPR spectra has been used for treatment of this contradiction. Quantitative agreement of simulated and experimental EPR spectra in the temperature range 77–300 K has been achieved simply by using the model of quasi-libration. By this term we mean that the probe molecules are in stochastic fast angular motion in the anisotropic cage of the matrix. The average angular displacement at ~ 300 K has been estimated as $5\text{--}15^\circ$.

Introduction

The spin probe method is widely used for estimating molecular rotational correlation times in various media: liquids and liquid crystals,^{1,2} biological objects,³ polymers^{4–8} etc. The method is based on consideration of the EPR spectra of stable free radicals with anisotropic magnetic parameters, commonly nitroxides. Averaging of the anisotropic constants induced by rotational motions manifests itself in variation of the shape of the EPR spectrum. Information on the mechanism of reorientation and correlation times is obtained from comparison of experimental and theoretically calculated spectra.⁹ The simple empirical relationships between the rotational correlation time and measured parameters of experimental spectrum (line width of components and outermost extrema separation, Fig. 1) have been extracted from calculated spectra.^{9,10} These relationships are widely used for estimation of correlation times from experimental EPR spectra because of their simplicity.

The spin probe method for fast rotational motions (correlation time $t_c < 10^{-9}$ s) gives results which are in agree-

ment with NMR and dielectric relaxation data. However, the method for slow reorientations is markedly less reliable. The sensitivity of EPR spectrum shape to slow motions is not so high. Inhomogeneously broadened spectra are often observed in experiments, and line width becomes insensitive to molecular motion in these conditions. Theoretical simulation of the shape of “slow motional” spectra is more complicated and does not result in good agreement with experimental spectra. It is in this field of mobility that correlation times obtained by different techniques differ. Particularly large discrepancies are observed for polymeric media in the vicinity of and below the glass transition temperature T_g . In this case, the difference in correlation time may be as much as 4–8 orders of magnitude.^{6–8} Such differences are ordinarily explained by the various sensitivities of different techniques to α and β relaxation processes in polymers.

Another type of molecular motion in glasses was the subject of extensive investigation during recent years.^{11–21} It is a small-angle stochastic motion limited by surrounding molecules. This motion, which is referred to as libration, has been found in low-temperature glasses^{11,12} as well as in polymers^{13,14} at low temperature using methods based on spin echo effect and magnetization transfer.

It should be emphasized that the libration in crystals differs essentially from the reorientational motion named libration in glassy media. Conventional librations in crystals are harmonic oscillations with frequency *ca.* $10^{11}\text{--}10^{12}$ s⁻¹ and amplitude less than $1\text{--}2^\circ$. The stochastic librations of nitroxides in glasses were found to be characterized by correlation times of about $10^{-9}\text{--}10^{-10}$ s and amplitude $< 5\text{--}10^\circ$.^{11–14}

The libration, as well as rotational motion, must cause the partial averaging of magnetic parameters and show itself in the spectrum shape. As the libration amplitude increases with the temperature, the experimentally determined magnetic parameters should be temperature dependent. The temperature dependence of the effective magnetic parameters below T_g is observed in experiments.^{15,16}

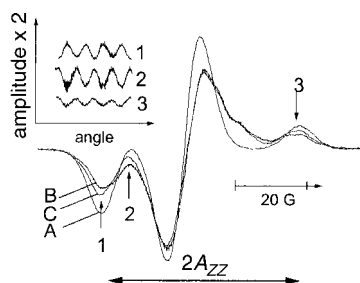


Fig. 1 EPR spectra of di-*p*-anisyl nitroxide in polystyrene before irradiation (A) and after 365 nm polarized irradiation (B, C) recorded at 77 K with perpendicular and parallel orientation of the sample axis to the direction of the magnetic field, respectively. Insert shows the angular dependence of the signal in points 1, 2, 3 of the spectrum.

Complex motion combined from anisotropic in-cage motion similar to libration and simultaneous slow reorientation of cage has been found in the vicinity of glass transition temperature of matrixes using high-frequency EPR.^{17–21}

Thus, two models—(a) low-amplitude librations with conservation of equilibrium space orientation and (b) slow molecular reorientations in isotropic media—can be used for explanation of the EPR spectra variation with temperature in glassy matrices. The present work is intended to discriminate between these models. It seems to be important to find the temperature regions of libration and true reorientation of guest molecules in polymers. This problem is attacked by using the photoselection phenomenon.^{22–24} Photoselection is described as a process in which the sample's anisotropy appears due to irradiation by polarized light. This is a result of different probabilities of light absorption and consequently of reaction of molecules with different orientations with respect to the electric vector of light. Unreacted molecules after irradiation of the rigid sample are ordered. This order may be viewed as light-induced linear dichroism or angular dependence of the EPR spectrum. The heating of the sample with the aligned paramagnetic centres and measurements of anisotropy provide a way of monitoring the molecular rotational mobility. The light-induced anisotropy should vanish at the sufficiently high temperature when the time scale of molecular reorientation is comparable with the timescale of experiment. The similar method of oriented spin probe was used for investigation of super-slow rotational relaxation in glasses.^{25,26}

Photoselection of di-*p*-anisyl nitroxide in glassy solutions at 77 K has been previously observed under polarized 365 nm irradiation.²⁷ In this connection di-*p*-anisyl nitroxide was selected as a probe in the present work. Oriented spin probe method gives additional information that should be compared with the data of ordinary spin probe method. It is important that both approaches may be applied to the same probe particle and matrix under identical conditions.

Experimental section

Experimental methods

Di-*p*-anisyl nitroxide was prepared and purified according to procedure.²⁸

95% ethanol, toluene and isopropylbenzene were used as glass-forming liquids. Polystyrene ($T_g \sim 370$ K), poly-*(N*-vinylpyrrolidone) ($T_g \sim 420$ K) and polyvinyl butyral ($T_g \sim 330$ K) have been chosen as they do not react with di-*p*-anisyl nitroxide. 4,4'-Dimethylbenzophenone was used as the crystalline matrix.

The samples of low-temperature glasses with di-*p*-anisyl nitroxide were prepared by dissolving the di-*p*-anisyl nitroxide in solvent immediately prior to use. The quartz ampoule (diameter 3 mm) with the solution was immersed in liquid nitrogen.

4,4'-dimethylbenzophenone with di-*p*-anisyl nitroxide embedded in crystal lattice was prepared by crystallization from ethanol solution.

Polystyrene films (thickness 200 μm , concentration of di-*p*-anisyl nitroxide $\sim 2 \times 10^{-3}$ M) were prepared by evaporation of benzene from a mixed solution of polystyrene and di-*p*-anisyl nitroxide with subsequent evacuation of the film at 10^{-3} Torr for 24 h. The polyvinylpyrrolidone and polyvinyl butyral films were prepared similarly using chloroform as a solvent. The absence of strain in the prepared films was controlled using a polariscope. Photolysis was performed with mercury high pressure lamp 500 W. The desired irradiation wavelength was obtained using standards glass filters. A Glan prism was used for photolysis and spectrophotometry measurement with polarized light.

The desired temperature (77–400 K) was kept by nitrogen vapour flow cryostat with an accuracy of $\pm 2^\circ$. The samples reached the temperature of the cryostat in no more than 100 s. The EPR spectra were recorded using a Varian E-3 spectrometer (X-band). Optical absorption spectra were registered by a Specord M-40 spectrophotometer.

Light-induced anisotropy of samples was observed as a linear dichroism or angular dependence of EPR spectra. The measurements of the orientation degree were carried out in ampoules with square cross section 2×2 mm as well as in circular ampoules. The orientation degree in the square ampoules was $\sim 10\%$ more than in the circular ones. Optical measurements are more accurate, but it is possible just for transparent samples. Cracking of glasses and films caused by the variation of temperature restricts the applicability of the optical registration.

Linear dichroism values were calculated at the wavelength of the maximum UV band of the radical (333–340 nm) in accordance with the expression:

$$d = \frac{D_{\perp} - D_{\parallel}}{D_{\parallel} + 2D_{\perp}}$$

where D_{\parallel} and D_{\perp} are the amplitudes of the absorption band of the spectra recorded with parallel and perpendicular mutual polarization of irradiating and probe beams of light, respectively (Fig. 2). The relative degree of orientation was calculated as a function of temperature from optical measurements as:

$$a_{\text{UV}}(T) = \frac{d_T}{d_{77}}$$

The light-induced angular dependence of the EPR spectrum was empirically characterized by the difference of amplitudes of the spectrum components measured at parallel and perpendicular mutual orientations of the magnetic field direction and the direction of the light polarization: $h_{\parallel} - h_{\perp}$. The more correct expression²⁹ cannot be used in this case due to the overlapping of the EPR spectra of the initial radical and the radical product of the photoreaction.

It should be emphasized that photoinduced anisotropy of the initially isotropic samples always has uniaxial symmetry. The sample's unique axis coincides with the electric vector of plane-polarized irradiating light.

The most accurate values of $h_{\parallel} - h_{\perp}$ are obtained if the amplitude of signal is measured as a function of angle between the sample axis and magnetic field. In our experiments the sample was continuously rotated with a frequency of 2 revolutions min^{-1} , and signal amplitude was recorded at the fixed magnetic field. The angular dependencies obtained at the different field points are shown in Fig. 1. The amplitude of the

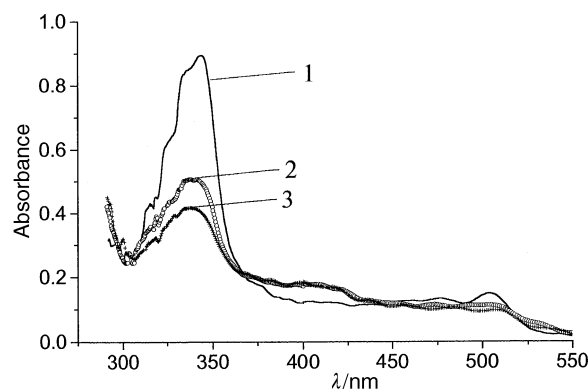


Fig. 2 UV spectra of di-*p*-anisyl nitroxide in ethanol glass at 77 K before irradiation (1) and after 365 nm polarized irradiation (2, 3) recorded with perpendicular and parallel polarization of the probing beam relative to the polarization of the irradiating one, respectively.

angular dependence is a desired measure of radical alignment. The relative degree of orientation measured by EPR at the different temperatures was calculated as:

$$a_{\text{EPR}}(T) = \frac{(h_{\parallel} - h_{\perp})_T}{(h_{\parallel} - h_{\perp})_{77}}$$

Computational methods

The shape of EPR spectra of the radical probe after photoselection was calculated earlier.^{27,29} In this work the simulated spectra for unirradiated isotropic sample are discussed only.

The EPR spectra of radicals fixed in the rigid matrix (rigid limit) were simulated at the strong field approximation. It was checked previously, that the nuclear Zeeman coupling has no effect on the shape of the calculated spectrum. The most general shape of individual line—a convolution of Lorentz and Gauss line—was used. The half-width of Lorentz and Gauss functions could be given as a tensor with the axes coincident with the axes of the g -tensor.

EPR spectra of spin probes in the slow motional regime were simulated with the Freed program (version 1.6).³⁰

To determine the effective magnetic and motional parameters, nonlinear least-squares fitting of the simulated spectra to the experimental ones was used. The sum of square deviations of a computed spectrum from an experimental one was minimized using an adaptive least-squares algorithm.^{31,32} The procedure converged to the same best-fitted set of parameters when starting values varied in reasonable limits.

In the course of the treatment of fixed radicals the effective components of the g -tensor and the tensor of hyperfine interaction (A -tensor) as well as the individual line parameters were varied. The starting set of parameters was taken from the literature.³³ The obtained best-fitted set contains the magnetic values averaged by fast librations.

During the simulation of the slow-motion spectra values of magnetic parameters were kept constant. They were taken from the optimal set of magnetic parameters describing the spectrum at 77 K. Least-squares fitting was performed with variation of rotational correlation times, direction of rotational axes in the molecular frame and line shape parameters as well as models of rotational motion.

Dispersion of the resulting parameters was calculated from elements of the covariation matrix. It was found that the agreement of computed and experimental spectra cannot be significantly improved when the discrepancy of g - and A -axes directions is taken into account.

Results

Results of experiment

Photochemical reaction of di-*p*-anisyl nitroxide in glassy solutions and films at 77 K has been observed earlier in the course of 365 and 436 nm light irradiation.²⁷ The quantum yield of reaction is about 10^{-4} . The primary product of the photochemical reaction is likely to be an aminyl-type free radical R- \dot{N} -O-R which is an isomer of the initial nitroxide. The product is unstable and decays with loss of spin on heating of the sample. Photochemical reaction in the matrix at 77 K proceeds with the conservation of the number of spins both in the presence and in the absence of dissolved oxygen. The EPR spectrum of the radical product overlaps with the central band of the initial radical spectrum. The alignment of the unreacted molecules of di-*p*-anisyl nitroxide is observed after 365 nm polarized irradiation. Fig. 2 shows the UV-VIS spectra recorded with the probe beam polarized parallel and perpendicular to the polarization of the irradiating one. The alignment of di-*p*-anisyl nitroxide radicals in irradiated

samples was observed as an angular dependence of EPR spectra too. The electric transition dipole moment μ in di-*p*-anisyl nitroxide does not coincide with the Z -axis of g -tensor. The direction of μ is close to the Y -axis of the magnetic frame of the molecule,²⁷ so the light-induced angular dependence of the outermost components corresponding to A_{zz} is not large. The greatest relative change of an EPR signal is observed in the area between the first and the second components of the spectrum (Fig. 1).

The anisotropy of sample induced at 77 K relaxes at higher temperature. Figs. 3 and 4 demonstrate the results of the following experiments. The sample irradiated at 77 K was held for 5 min at the specified temperature. Then the sample was recooled to 77 K, and the orientation degree of the probe was measured at this temperature. Fig. 3 shows that the temperature range of rotational relaxation detected by linear dichroism and angular dependence of EPR spectra is 220–300 K. However, one can see that the orientation degrees a_{EPR} and a_{UV} measured by the different methods are differ. This discrepancy will be discussed below.

One can see that the EPR spectra show some increase in the degree of orientation with rise of temperature in the low-temperature part of curves (Fig. 4). This rise is particularly detectable in low-temperature glasses. The EPR spectra demonstrate the chemical transformations of the initial product of the photochemical reaction in the same temperature range. Thus, the apparent increase of the orientation degree is caused by the disappearance of the contribution of the product alignment that is complementary to the alignment of the probe molecules. The contribution of product alignment

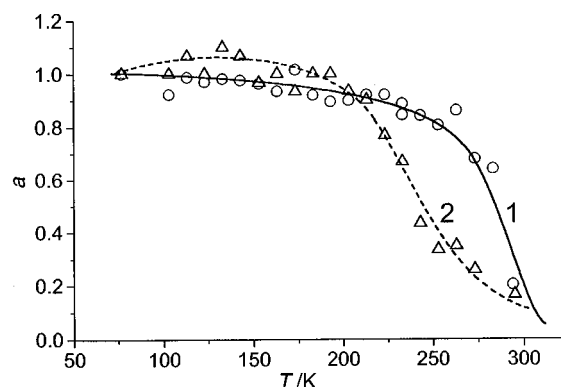


Fig. 3 Dependencies of relative orientation degree measured by linear dichroism (1) and EPR spectra (2) of irradiated sample of di-*p*-anisyl nitroxide in polystyrene matrix from temperature.

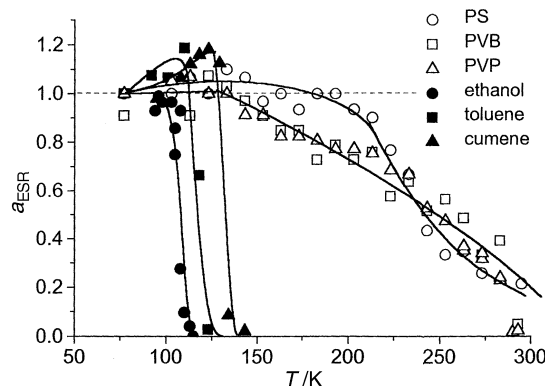


Fig. 4 Temperature dependencies of relative orientation degree measured by EPR spectra of samples of di-*p*-anisyl nitroxide in ethanol (solid circles), toluene (solid squares), isopropylbenzene (solid triangles), polystyrene (open circles), polyvinyl butyral (open squares) and poly-(*N*-vinylpyrrolidone) (open triangles).

influences the angular dependence of the EPR spectra since the spectra of the initial probe and the photoproduct overlap.

The relaxation of alignment in low-temperature glasses occurs within a narrow temperature range of less than 5° (Fig. 4). Step-type relaxation (Fig. 5) over a temperature range as large as 150° is observed in the polymer matrices. Each point on Fig. 5 was obtained by holding the sample at a particular temperature, recoiling to 77 K and registration of spectra. The abscissa on Fig. 5 is the total time of holding.

The irradiation of the radical probe in polystyrene and polyvinyl butyral films at room temperature gives ordered samples as well as low temperature irradiation. The degree of orientation of the samples irradiated at room temperature is less than of those irradiated at 77 K.

For comparison purposes the rotation correlation times have been measured in the same systems using the well-known spin probe technique.⁹ The EPR spectra of the isotropic unirradiated samples were recorded at the different temperatures.

The EPR spectra of di-*p*-anisyl nitroxide embedded in crystals of 4,4' dimethylbenzophenone were recorded in the temperature range 77–373 K. The spectrum shape was found to be nearly constant. The line width was only slightly temperature dependent. The variations of the magnetic parameters were within experimental error.

Unlike the crystals, in a polystyrene matrix, temperature dependence of EPR spectra is observed. Fig. 6 demonstrates the temperature dependence of outermost extrema separation in the spectra of di-*p*-anisyl nitroxide in polystyrene. Rotation correlation time is obtained as follows:

$$\tau = a(1 - S)^b$$

where $S = 2A'_{zz}/2A_{zz}$, where $2A_{zz}$ and $2A'_{zz}$ are the outermost extrema separation in the spectrum recorded at 77 K

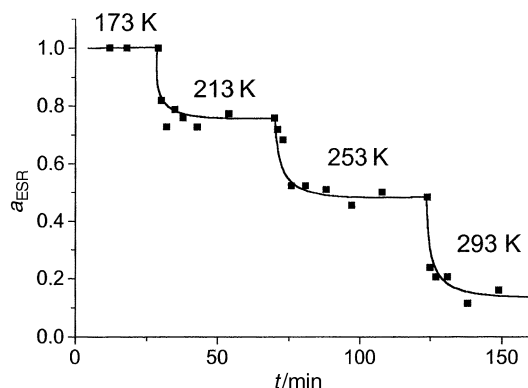


Fig. 5 Orientational relaxation of light-induced alignment of di-*p*-anisyl nitroxide in polystyrene at the stepped heating (EPR measurements).

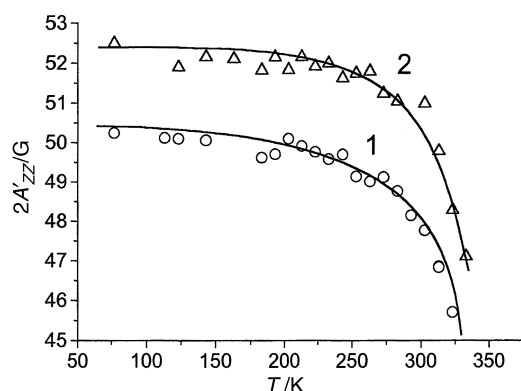


Fig. 6 Temperature dependence of outermost extrema separation ($2A'_{zz}$) in EPR spectra of di-*p*-anisyl nitroxide in polystyrene (1) and polyvinyl butyral (2).

(rigid limit) and that at the particular temperature, respectively, and a and b are the empirical parameters given in ref. 9.

Maximal detectable times for this technique are about 10^{-7} s. These times correspond to the beginning of change in $2A'_{zz}$ on increasing the temperature. This temperature for polystyrene matrix is approximately 250 K.

Results of EPR spectra simulation

The typical results of the simulation of the EPR spectra for polystyrene matrix in terms of the model of slow reorientation in isotropic medium are presented on Fig. 7. The Brownian reorientation correlation time and individual line width were varied in the course of the simulation to obtain the minimum of deviation of the computed spectrum from the experimental one. The results can be summarized as following:

(1) The EPR spectra at the low temperature are weakly temperature dependent. The reorientations do not have much influence on the spectra's shape. That is, the spectra have essentially the same shape as at 77 K. The best-fitted spectra are in good agreement with experiment.

(2) The larger is the departure of an experimental spectrum from the spectrum at 77 K, the poorer is the agreement between computed and experimental spectra. Quantitative description can not be achieved at the fixed magnetic parameters. Above approximately 240 K, both the shape and the positions of components in the best-fitted spectra differ noticeably from experimental ones.

(3) The optimal rotation correlation times obtained in the course of the fitting are in the range 10^{-7} – 10^{-8} s at all temperatures.

(4) The variation of the motional model (anisotropy of rotation, jump model, etc.) does not result in essential improvements of the agreement between computed and experimental spectra.

Thus, simulation of the temperature dependence of EPR spectra gives the same correlation times as a qualitative empirical analysis. It should be concluded, however, that the model of reorientation in isotropic media is inadequate as the simulated spectra are in disagreement with the experimental ones.

Typical results of the simulation of EPR spectra of the radical fixed in matrix (libration model) are shown on Fig. 8. In the course of this simulation procedure the magnetic parameters of the radical are varied. The optimal magnetic parameters corresponding to the best-fitted spectra are the effective parameters averaged by fast low-amplitude orienta-

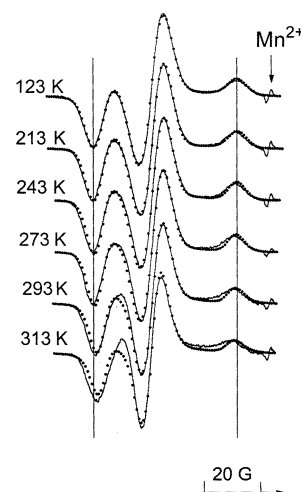


Fig. 7 Experimental EPR spectra of di-*p*-anisyl nitroxide in polystyrene at the different temperatures (lines) and best-fitted spectra obtained using the model of Brownian reorientation in isotropic media (points).

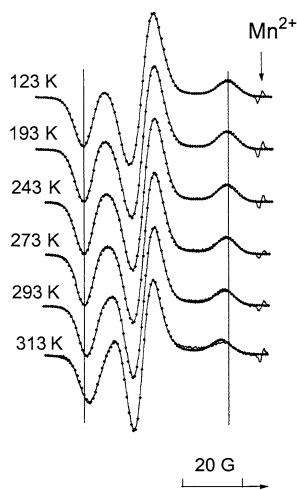


Fig. 8 Experimental EPR spectra of di-*p*-anisyl nitroxide in polystyrene at the different temperatures (lines) and best-fitted spectra obtained using the model of quasi-librations (points).

tional motion. One can see the better quantitative agreement of computed and experimental spectra up to ~ 300 K (Compare, for example, the spectra at 293 K on Fig. 7 and Fig. 8). Temperature dependence of obtained effective magnetic parameters is shown on Fig. 9.

Discussion

The results presented above show that the rotational mobilities of spin probes in crystals, low-temperature glasses and polymer glasses differ fundamentally. True harmonic libration in a crystal lattice does not show itself in X-band EPR spectra. The stochastic librations with larger amplitude occur in low-temperature glasses. Librations are reflected in weak tem-

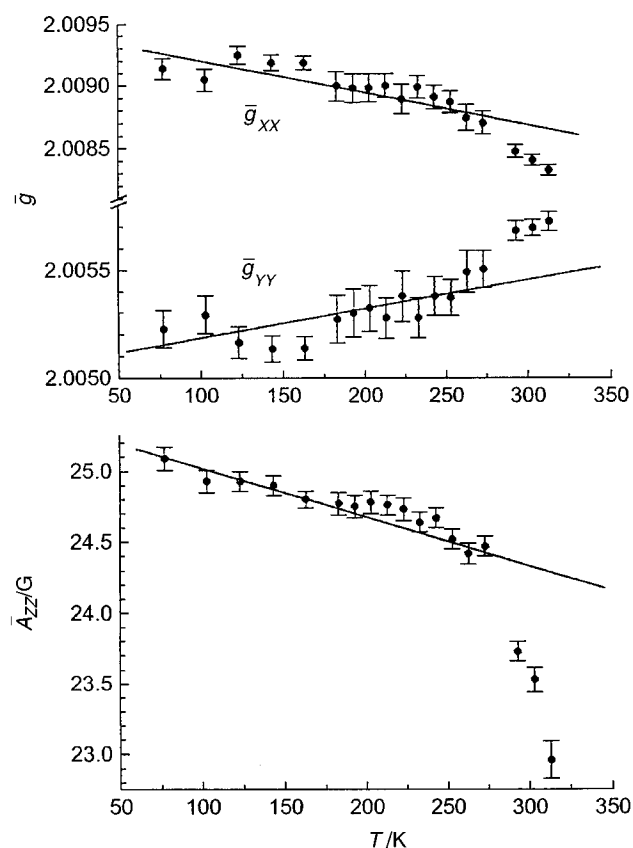


Fig. 9 Temperature dependencies of effective magnetic parameters of di-*p*-anisyl nitroxide in polystyrene obtained by the nonlinear least-squares fitting of experimental spectra.

perature dependence of the effective magnetic parameters. A sharp increase of the amplitude of the rotational motions is found in the vicinity of T_g where both the relaxation of induced alignment and strong changes of EPR spectrum are observed.

Temperature dependence of rotational mobility in polymer matrices should be divided in three parts. The rotational behavior of radical in the low temperature part of dependence (77–150 K for investigated polymers) is similar to the one in low-temperature glasses below T_g . The relaxation of alignment is not observed in this temperature range and, hence, the possibility of true reorientation is eliminated.

The librations of the guest molecules in the rigid media have been widely discussed in literature.^{11–20} It is known that libration amplitude can be estimated from the temperature dependence of effective magnetic parameters.^{15,16} Formulas corresponding to averaging of magnetic parameters have been obtained on the assumption of limited rotational motion around the one axis or coincident with the principal magnetic axis³⁴ or arbitrary directed in the molecular frame.³⁵ These models are seen to be too simplified. Obviously the libration is the simultaneous rotational motion around three mutually perpendicular axes. As directions of these axes are not known, we assumed the principal axes of *g*-factor to be the main axes of librations. It seems likely, that this assumption has a little influence on results of averaging as the three rotations around any set of axes produce the averaging of all magnetic parameters. The formulas corresponding to this model can be easily obtained by the application of the averaging procedure described in ref. 34 to all axes sequentially:

$$\begin{aligned}\bar{A}_x &= A_x + (A_z - A_x)S_y + (A_y - A_x)S_z \\ \bar{A}_y &= A_y + (A_z - A_y)S_x + (A_x - A_y)S_z \\ \bar{A}_z &= A_z + (A_y - A_z)S_x + (A_x - A_z)S_y\end{aligned}\quad (1)$$

where \bar{A}_x , \bar{A}_y and \bar{A}_z are the effective (averaged) hyperfine constants, $S_x = \langle \sin^2 \alpha_x \rangle$, $S_y = \langle \sin^2 \alpha_y \rangle$ and $S_z = \langle \sin^2 \alpha_z \rangle$, and α_x , α_y and α_z are the angles of rotary displacement around *x*, *y* and *z*, respectively. The components of the effective *g*-tensor are defined by equations having exactly the same form as eqn. (1). For low-amplitude motion the $\sin \alpha$ may be replaced by α and one can determine the mean squared values of angular displacements $\langle \alpha_x^2 \rangle$, $\langle \alpha_y^2 \rangle$, $\langle \alpha_z^2 \rangle$ from the temperature dependence of effective magnetic parameters, angle brackets indicate the averaging on all displacements. It was found that these values for temperature 150 K correspond to angular displacements in the region of 2–4°.

The second range of temperature dependence is approximately 150–300 K. Both strong temperature dependence of EPR spectra and stepped relaxation of alignment are observed in this temperature range. The EPR spectra shape can only be quantitatively fitted if the approximation of fixed radicals is adopted. Using eqn. (1) and the temperature dependence of the effective magnetic parameters (Fig. 9) it was found:

$$\begin{aligned}\langle \sin^2 \alpha_x \rangle &= 0.008 \\ \langle \sin^2 \alpha_y \rangle &= 0.020 \\ \langle \sin^2 \alpha_z \rangle &= 0.077\end{aligned}$$

The error of determination of these values is rather high. It depends on the error of effective magnetic parameters and the rate of their changing with temperature. The results are slightly changed with the variation of magnetic parameters determination procedure. Nevertheless, in all cases the averaged angular displacements are in the range ~ 5 –15°.

The relaxation of radical alignment in polymers on the time scale of minutes is observed in the temperature range 150–300 K. This relaxation is obviously explained by a slow reorganization of cages with the changing of its spatial directions. This reorganization proceeds in a step-type manner (Figs. 4 and 5).

The step-type processes in polymers are conventionally explained by distinct properties in different points of polymers, in other words by wide distribution of molecules over the characteristic time. An alternative explanation is the model of correlated cage reorganization in polymer, when the more the angle of turn, the bigger is the activation energy of this turn. Experimental stepped relaxation can be associated with both of these explanations. However, the second explanation is preferential from our point of view.

Evidence against the wide distribution over rotational time is the difference between the two relaxation curves shown on Fig. 3. This difference is not surprising in the context of the model of correlated relaxation. It should be taken into account that the directions of optical transition and magnetic axes of probe do not coincide. In this case, orientation degrees measured by optical and EPR spectroscopy characterize the different orientation distributions, orientation distribution of transition dipole axes of the radicals (μ -axes) and orientation distribution magnetic axes (primarily Z -axes) of the radicals, respectively. These two distributions differ in shape as the polarized light induces the alignment of probe molecules according to their μ -axis but the Z -axis makes an angle with the μ -axis. The molecular motions around different axes are restricted in varying degrees. Hence, the distribution of μ -axes of radicals and distribution of their Z -axes variously change in the course of molecular reorientation. The measured values of orientation degree are the averaged characteristic of orientation distribution. So, it is clear that relaxation curves measured by different techniques can be different. Nevertheless, both methods give the temperature range of relaxation to be on the time scale of minutes.

The relaxation curves obtained with different methods should coincide in the case when the probe molecules may be divided into two sorts: fast rotating molecules and fixed molecules. The relaxation curve in this situation would reflect fractions of fixed molecules. This is a condition of wide distribution of probe molecules over the rotational time. So, experimental results argued against this model.

The second argument against the wide distribution lies in the shape of EPR spectra. It is known that the distribution over rotational time manifests itself as a "composite" EPR spectrum containing the motionally narrowed lines and broadened spectrum of "frozen" particles (see, for example ref. 21). Spectra with these features are not found in the experiment.

The third range (> 300 K) in the temperature dependence in polymer matrices is characterized by strong variation of EPR spectra shape and lack of long-lived light-induced alignment. EPR spectra shape can not be simulated quantitatively either in the model of fixed radicals or in the model of reorientation in an isotropic medium. It means that the motion in the cage does not average the magnetic parameters. *i.e.* the angular amplitude is too large and the frequency of motion is not high enough for averaging of magnetic parameters. So, the frequency can be concluded to be about 10^8 – 10^9 s $^{-1}$.

To summarize it should be concluded that reorientational motion of spin probe molecule in glassy polymers is more restricted than was considered previously. The model most appropriate to experimental results is the following one. The cage in the glassy matrix is an anisotropic one. The walls of the cage restrict the intracage rotational motion of the guest molecules. Amplitudes and correlation time of these motions in polymers show that the cage walls fluctuate conserving the average shape and direction of cage. Rotational intracage motion of the spin probe molecule is likely to be *via* joint displacement of radical and matrix fragments. The role of these displacements rises with temperature.

The amplitude of the rotational motion of spin probe in the cage of polymer is rather large. It casts doubt on the correctness of using the term "libration", as this term is commonly

used for low-amplitude motion. In this context we use the term "quasi-libration" which denotes the high-amplitude stochastic motion. It seems likely that the quasi-librations gradually transform into Brownian reorientation when the temperature is increasing.

The cage of low-temperature glass is a rigid one up to the glass transition temperature. At the temperatures above T_g , the characteristic time of cage reorganization becomes too small to record in our experiment. Unlike low-temperature glasses, the polymer matrices are characterized by a wide set of relaxation times. In glassy polymers the shape and space orientation of cage changes slowly. The characteristic time of this change is about a minute for polymers investigated at room temperature. The reorganization of the cage appears in experiment as the relaxation of light-induced alignment. This model is similar to the model of "slow relaxing local structure" used in ref. 20 for the detailed description of the 250 GHz EPR spectrum of nitroxides in toluene at the temperature -128 °C. The distinction lies in the fact that the time of cage reorganization obtained in ref. 20 is only one order of magnitude more than the characteristic time of intracage motion. In our experiments the difference between intracage motion time and cage reorganization time is 10 orders of magnitude.

Conclusion

The rotational mobility of the di-*p*-anisyl nitroxide spin probe in glassy matrices has been studied by a direct method, namely by measurements of temperature dependence of rotational relaxation of light-induced alignment of probe molecules. The rotational relaxation in low-temperature glasses was found to occur in the vicinity of glass transition temperature T_g . The stepped relaxation of alignment on a time scale of minutes has been found in the temperature range 150–300 K for polystyrene, poly(*N*-vinylpyrrolidone) and polyvinyl butyral. Rotational correlation times *ca.* 10^{-6} – 10^{-7} s, which have been obtained before in these conditions, are concluded to be incorrect.

The temperature dependence of the shape of EPR spectra explained earlier in terms of molecular motion in isotropic media has been examined using the nonlinear least-squares fitting of experimental spectra. The model of reorientation in isotropic media provides no way of quantitative simulation of EPR spectra below the glass transition temperature of polymer. The quantitative agreement of simulated and experimental EPR spectra in the temperature range 77–300 K has been achieved just using the model of quasi-libration when the probe molecules are in stochastic fast angular motion in the anisotropic cage of the matrix. The angular displacements in the course of this motion are restricted by cage shape. The averaged angular displacement at ~ 300 K was found to be 5–15°.

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