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Rotational mobility and rate of photoisomerization of spin-labeled azobenzenes in glassy polystyrene

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ABSTRACT

The rate of photochemical isomerization of azobenzene derivatives dispersed in glassy polystyrene has been measured along with rotational mobility of reacting molecules. For this purpose bifunctional probe molecules carrying a paramagnetic nitroxide fragment and a photochromic azobenzene moiety were used. The kinetics of photoisomerization was followed by monitoring the change in the UV–Vis absorbance spectra. Rotational mobility was determined by numerical simulation of the ESR spectra. It has been shown that in the matrix of glassy polystyrene amplitudes of high-frequency angular displacements (quasi-librations) correlate with the rate of photochemical *trans–cis* isomerization.

1. Introduction

An appreciable amount of data found in the literature confirms that restricted rotational mobility of molecules in solid materials can significantly influence the rates of solid-state chemical reactions [1–4]. At present, however, no model can offer a quantitative relation between rotational mobility and reaction rate in the solid state. A serious obstacle for creating such a model is the fact that in most cases rotational mobility is determined indirectly. Commonly the rotational mobility is characterized on the basis of the relaxation spectrum of the medium [5] or the dynamics of an additional molecular probe placed in the medium [6]. Rotational mobility and reaction rates of reagent molecules were determined simultaneously in very few cases, namely, for intramolecular fragment transfer in ortho-semiquinone radicals [7–9], for spin exchange in nitroxide biradicals [10], and for a series of bimolecular reactions of nitroxide radicals [11–13]. These data are summarized in a review [4]. This research dealt with reactions in viscous solutions or plasticized polymers in rubbery or viscous-flow states. The rotational correlation times of reacting molecules were in the range of 10^{-8}–10^{-10} s. Under these conditions, linear dependence between characteristic time of reaction and rotational correlation time was observed. For azobenzene-containing copolymers it was shown [14] that the rate constant of thermal cis–trans isomerization correlates with the frequency of a certain dielectric relaxation process, attributed to orientational movements of azobenzene moieties.

Until now, no quantitative data is present concerning the relation between photochemical reaction rates and rotational mobility of reagents in the solid state. One of the main difficulties in obtaining such data is the lack of techniques for determination of rotational mobility in solids. In most cases the model of rotational diffusion fails to describe rotational mobility. However, an alternative model has been proposed recently. It has been shown [15–18] that molecules dispersed in glassy materials undergo fast quasi-librations. These are restricted angular movements, which possess the spectrum of characteristic times in the range of 10^{-10}–10^{-12} s. Amplitudes of these motions can be readily obtained from 3 cm ESR spectra. The lifetimes of photoexcited molecules lie in a similar time range. Therefore, one can expect that a relationship exists between the intensity of rotational motions of molecules in solids and the rate of their photochemical transformations.

To reveal this relationship we have used bifunctional probe molecules, which contain a photoisomerizable azobenzene fragment and a nitroxide fragment, which serves as a spin label.

2. Experimental

The structures of the probes used in this work, are presented in Figure 1. The probes were synthesized by Prof. Sh. Nakatsuji, as described in [19]. Atactic polystyrene, used as a polymer medium, was purified from low-molecular impurities by precipitation.

Polystyrene films, doped with spin probes, were cast from benzene solutions. The thickness of the films was about 0.2 mm, the probe concentration was 0.001–0.003 mol l^{-1}. In these conditions dipole–dipole broadening of ESR spectra is negligible. The films were dried in air for at least a week, then in vacuo (10^{-3} Torr) for another week to fully remove benzene. A sample of the film was placed in a quartz ampoule, evacuated to 10^{-3} Torr and sealed. Then the sample was annealed at 363 K for 2 h to standardize the thermal history.

Optical spectra were recorded using Specord M40 UV–Vis spectrometer. ESR spectra were recorded with an X-band ESR

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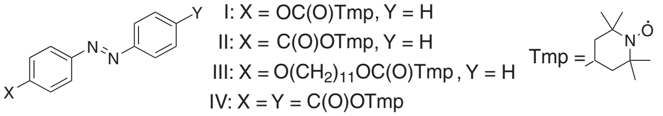

Figure 1. Structures of bifunctional probes, used in this work.

spectrometer Varian E-3. The magnetic field sweep was calibrated on the third and the fourth components of ESR spectrum of Mn^{2+}/MgO. Absolute values of *g*-factors were determined using an additional external standard, (N, N)-diphenyl-N′-picrylhydrazyl, with the known *g*-factor value 2.0037 ± 0.0001.

The procedure for the numerical simulation of ESR spectra is described elsewhere [15,17,18]. Spin-Hamiltonian parameters of probes I–IV in glassy polystyrene were determined by simulating their lowest-temperature ESR spectra (recorded at 77 K for I–III, and at 103 K for IV). In the course of the simulation, the three principal values of *g*-tensor were subjected to a constraint:

$$\frac{1}{3}(g_{xx} + g_{yy} + g_{zz}) = g_{iso}$$

where g_{iso} is an isotropic *g*-factor for the given probe. Isotropic magnetic parameters were measured from the spectra of liquid solutions of the probes I–IV in 2-methyltetrahydrofuran. The values of spin-Hamiltonian parameters, as well as isotropic *g*-factors and hfs-constants, are presented in Table 1.

ESR spectra recorded at 103–353 K were simulated in the framework of a quasi-libration model. Quasi-librational motions around the three principal axes of *g*-tensor were determined separately. To account for each of these motions, the Griffith formulae [20] were used. Rotational mobility distribution of the probe molecules was accounted for as described in [18]. We used the modified Gaussian distribution of quasi-libration amplitudes, with the distribution density defined by

$$\rho(L; L_0, \sigma) = \begin{cases} \frac{1}{Q\sigma\sqrt{2\pi}} \exp\left(-\frac{(L-L_0)^2}{2\sigma^2}\right), & 0 \leqslant L \leqslant 90 \\ 0, \quad L < 0, & L > 90 \end{cases}$$

where L_0 and σ are the distribution center and width, $Q = N\left(\frac{90-L_0}{\sigma}\right) - N\left(-\frac{L_0}{\sigma}\right)$ - normalization factor, $N(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x} \exp\left(-\frac{\xi^2}{2}\right) d\xi$ – cumulative Gaussian distribution function.

The irradiating light was generated by a 500 W ultra-high pressure mercury-vapor lamp, equipped with a water IR filter and 365 and 436 nm glass color filters. The light intensity was determined using the ferrioxalate actinometry procedure [21]. The irradiated samples were thermostated in a flow of gas (nitrogen or air). The absorbance of the sample during photolysis was followed by the residual intensity of irradiating light, measured with a vacuum Sb–Cs photodiode.

Prior to kinetic measurements at each temperature, the sample was annealed at 293 K for 15 min to standardize its thermal history. Before recording of trans–cis isomerization kinetic curves, the samples were converted to trans-form by irradiation with 436 nm light at 113 K.

The kinetic curves were treated according to the kinetic model of photochromism, described in [22,23]. If the thermal cis–trans conversion is negligible, the change of absorbance at irradiating wavelength is given by

$$\ln \frac{D - D_\infty}{D_0 - D_\infty} = -lI_0(\varepsilon_{trans}\varphi_{t\to c} + \varepsilon_{cis}\varphi_{c\to t}) \cdot \tilde{t} \tag{1}$$

where I_0 is irradiating light intensity, l is the polymer film thickness, D_0 and D are the initial and the current values of absorbance, ε_{trans} and ε_{cis} are the extinction coefficients of trans- and cis-isomers of the probe, $\varphi_{t\to c}$ and $\varphi_{c\to t}$ are the quantum yields of trans–cis and cis–trans isomerization, $\tilde{t} = \int_0^t \frac{1-10^{-D(\tau)}}{D(\tau)} d\tau$, D_∞ is the absorbance at the photostationary state, $D_\infty = c_0 l \varepsilon_{trans} \varepsilon_{cis}(\varphi_{t\to c} + \varphi_{c\to t})/(\varepsilon_{trans}\varphi_{t\to c} + \varepsilon_{cis}\varphi_{c\to t})$, c_0 is the total concentration of cis- and trans-isomers of the photochrome (all extinction coefficients and absorbances are at the irradiating wavelength).

3. Results and discussion

The structures of probe molecules used are presented in Figure 1. The probes contain nitroxide spin labels, attached to phenyl rings of azobenzene groups. In probes I and II, the two fragments are rigidly connected. The crystal structure data [19] show that the molecules of these substances are rod-shaped, with the length of about 17 Å. In probe III a flexible alkyl chain separates azobenzene and nitroxide fragments and allows some independent mobility of these moieties. The probe IV contains two spin labels per molecule, symmetrically attached to the two sides of azobenzene moiety.

A temperature dependence of ESR spectrum of probe II in glassy polystyrene is presented in Figure 2. The observed changes in spectra are typical for nitroxide probes in glasses. The temperature increase causes the outer extrema to draw together, and in addition some shape transformations in the central part of the spectrum take place. It is known [24–26] that such changes in the ESR spectra in glassy matrices are caused by quasi-librations. Quasi-librations are high-frequency (10^{10}–10^{12} Hz) but restricted to the amplitude stochastic angular displacements of probe molecules. It was shown [15–18] that taking into account these motions makes it possible to quantitatively describe temperature dependences of ESR spectra of spin probes in glasses. Therefore quasi-libration model was used to simulate the spectra in this work.

Since magnetic tensors of nitroxides are highly anisotropic, probe rotations around different molecular axes lead to specific changes in the ESR spectra. Therefore, simulation of such spectra may clarify rotational anisotropy of the probe. For this reason, in this work the amplitudes of quasi-librational motions around the three principal *g*-tensor axes were determined.

Simulations have shown that the quasi-libration model quantitatively describes the lowest-temperature spectra only. At temperatures higher than 150 K discrepancies between experimental and simulated spectra become significant. To expand the temperature range, in which the quasi-libration model is applicable to describe

Table 1
Spin-Hamiltonian parameters of probes I–IV, determined by simulation of ESR spectra in rigid limit, and isotropic spin-Hamiltonian parameters.

	I	II	III	IV
g_{xx}	2.00953 ± 0.00008	2.00958 ± 0.00005	2.00989 ± 0.00005	2.00902 ± 0.00007
g_{yy}	2.00645 ± 0.00007	2.00634 ± 0.00005	2.00657 ± 0.00005	2.00675 ± 0.00007
g_{zz}	2.00202 ± 0.00015	2.00209 ± 0.0001	2.00214 ± 0.00010	2.00226 ± 0.00014
A_{xx} (G)	7.58 ± 0.13	7.33 ± 0.09	7.30 ± 0.10	8.22 ± 0.09
A_{yy} (G)	5.77 ± 0.14	5.7 ± 0.1	5.75 ± 0.11	5.5 ± 0.1
A_{zz} (G)	33.62 ± 0.05	33.51 ± 0.03	34.17 ± 0.06	33.34 ± 0.02
g_{iso}	2.0060 ± 0.0002	2.0062 ± 0.0002	2.0062 ± 0.0002	2.0060 ± 0.0002
a_{iso} (G)	15.56 ± 0.05	15.49 ± 0.05	15.60 ± 0.05	15.27 ± 0.12

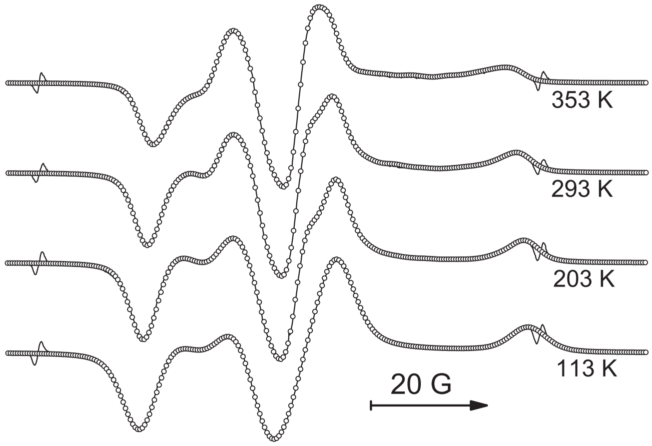

Figure 2. Temperature dependence of the ESR spectrum of probe II in polystyrene; experimental (lines) and best-fit simulated (circles) spectra are presented.

the spectra, the rotational mobility distribution of probe molecules should be taken into account [18]. Indeed, introduction of Gaussian distribution of libration amplitudes significantly improves the quality of fitting, and allows accurate reproduction of all ESR spectral shapes up to the glass transition temperature of the host polymer. In the range 150–250 K the fitting is successful even if the distribution center, L_0, is fixed at zero, which reduces the number of varied motional parameters to one per rotation axis. Thus, the account of rotational mobility distribution improves the quality of spectra simulation appreciably without increasing the number of varied parameters. The change of the distribution density with temperature is illustrated in Figure 3. The half-width of the distribution at 250 K is ca. 20°. The increase of temperature within the interval 250–350 K slightly narrows the distribution and shifts it to higher amplitudes.

Temperature dependences of averaged libration amplitudes are shown in Figure 4. Large errors at low temperatures originate from the broadening of the spectra due to an unresolved proton hyperfine splitting. The spectral line widths gradually decrease at 100–180 K, which can be attributed to the onset of rotations of methyl groups of the probes at these temperatures [27]. It is interesting to note that the onset of phenyl group rotations in polystyrene, as evidenced by dielectric relaxation measurements, also takes place at a close temperature ($T_\gamma \sim 180$ K) [28]. However, as seen in Figure 4, no dramatic changes in quasi-libration amplitudes at these temperatures can be observed.

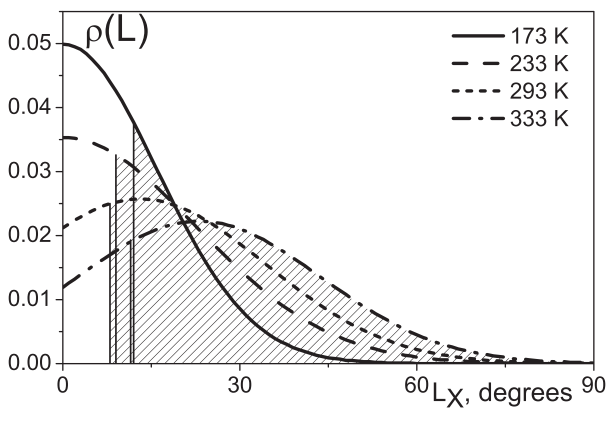

Figure 3. Temperature dependence of distribution density of quasi-libration amplitudes for probe II, determined as a result of numerical simulation of ESR spectra; hatching indicates photochemically active molecules (see text).

As can be clearly seen from Figure 4, quasi-librational motions of azobenzene probes I–IV are highly anisotropic. The most intensive are librations around the *x*-axis of the probe. This axis is directed along the N–O bond of the nitroxide fragment and is similar to the long inertia axis of the probe. This facilitates rotational movements around the *x*-axis. In a broad temperature range the account of quasi-librations around this axis alone is sufficient to quantitatively reproduce the spectra.

Quasi-librations around the *y*-axis emerge at 263 K for probes I and II, and at 213 K for probe III. Due to the broadening of the spectra it is impossible to resolve quasi-librations around *x* and *y* axes at high temperatures for sample IV. Librations around the *z* axis are determined with large errors, because they cause changes in the poorly resolved central part of the spectrum. At 103–353 K no librations around the *z*-axis can be discerned in the ESR spectra of probes I–IV. It is worth mentioning that, unlike azobenzene nitroxides I-IV, small spin probes with nearly spherical shapes were shown to undergo quasi-librations mainly around *y* and *z* axes [17,18].

Photochemical transformations of substances I–IV are related to their azobenzene fragments, capable of reversible photoisomerization. Photochromism of azobenzene derivatives in polymer media has been a subject of extensive research [2,29,30], which dealt both with polymers containing covalently linked azobenzene moieties [14,31–36] and azo dyes molecularly dispersed in the polymer [37–39]. Photochemical trans–cis and thermal cis–trans isomerizations were proven to be sensitive to the change of polymer mobility, which makes it possible to use azo dyes as molecular probes of free volume [35–37] and physical aging [34,35,37].

The photochemical behavior of the studied samples was found to be typical of azobenzene derivatives in polymers. Upon prolonged irradiation, a photostationary state is reached, in which the rates of trans–cis and cis–trans isomerizations are equal. Photostationary states, generated by irradiation with 365 and 436 nm light, are relatively enriched with cis- and trans- isomers, correspondingly. Our experimental data show that the rate and the final extent of trans–cis isomerization are essentially temperature dependent (Figure 5). On the contrary, the rate of cis–trans isomerization was found to be temperature independent. This peculiarity is common for isomerization of azobenzene derivatives in glassy polymers [38]. Its traditional explanation is based on the fact that the effective volume of cis-isomer is larger than that of trans-isomer. Consequently, cis–trans isomerization leads to the decrease of the effective volume and is therefore not hindered by the molecules of the medium.

A complication for the kinetic treatment of trans–cis isomerization is the non-exponential kinetics. Eq. (1) fails to fit the kinetic curves. Several explanations were proposed to account for the non-exponential kinetics in solid-state reactions [2,31,32,40,41]. We suppose that in our case it may be explained by the fact that chemically identical probe molecules may react with different probabilities, i.e. are kinetically inequivalent. This assumption is proven by the following experiment. When trans–cis isomerization is carried out at 129 K, upon prolonged irradiation, the reaction ceases at a certain degree of conversion. If, however, the irradiation is stopped, and the sample is annealed at 293 K for 10 min, then cooled down to 129 K and irradiated, the photochemical reaction resumes to achieve a higher extent of trans–cis isomerization. By interchanging irradiation at 129 K and annealing at 293 K, a step-like kinetic curve is obtained, with a new step after each annealing. The described phenomenon is explained as follows. During the annealing, the rearrangement of the local surroundings of probe molecules takes place. In the course of this rearrangement, a new fraction of molecules becomes available to isomerize at low temperature.

Thus, the kinetic experiments suggest that a distribution of isomerization reaction rates must exist in the polymer medium.

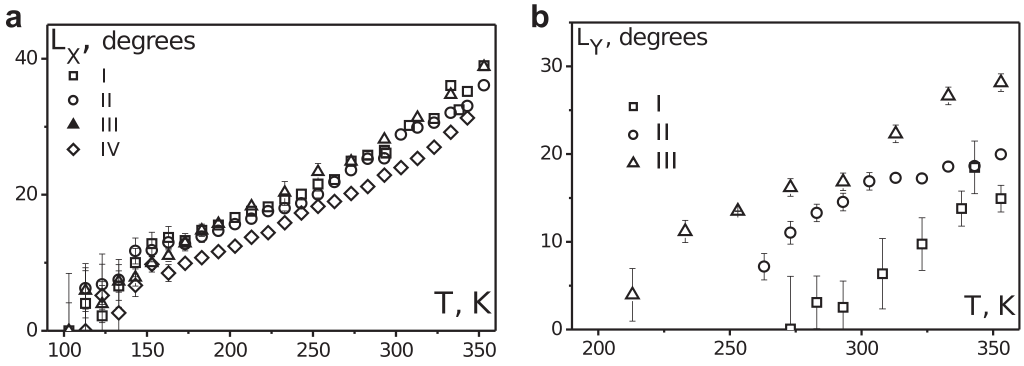

Figure 4. Quasi-libration amplitudes of probes I–IV around *g*-tensor axes *x* (a) and *y* (b), determined in the course of numerical simulation of ESR spectra.

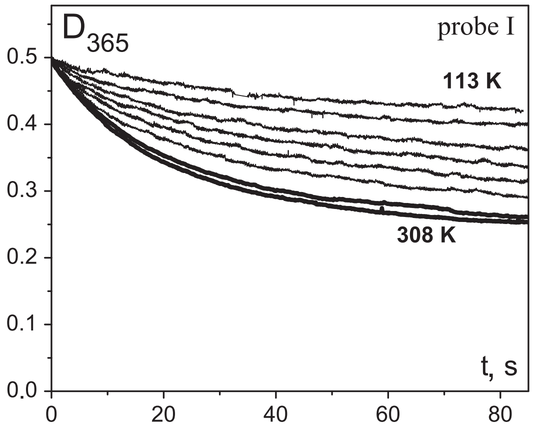

Figure 5. Kinetic curves of trans–cis isomerization of probe I in glassy polystyrene.

This result is in accordance with the existence of distribution of molecules according to their rotational mobility, discussed previously in this Letter based on the ESR data.

In the situation of kinetic inequivalence, kinetic measurements can only yield parameters averaged over the distribution. A convenient value is the initial slope of kinetic curves. If the reaction starts with a pure trans-isomer, this value is proportional to the average quantum yield of trans–cis isomerization:

$$\bar{\varphi}_{t\to c} = -\frac{1}{l^2 I_0 c_0 \varepsilon_{trans}(\varepsilon_{trans}-\varepsilon_{cis})}\cdot\frac{D}{1-10^{-D}}\bigg|_{t=0}\cdot\frac{dD}{dt}\bigg|_{t=0}$$

The quantum yields measured at 293 K for probes I, II and III were found to be 0.04 ± 0.02, 0.03 ± 0.02 and 0.05 ± 0.01, respectively, and for probe IV – an order of magnitude lower, 0.003 ± 0.002. Large errors result from the uncertainties of extinction coefficients of cis-isomers. To eliminate these errors, in this work we use relative quantum yields, equal to the ratio of initial slopes of kinetic curves:

$$\bar{\varphi}^{T}_{t\to c}\Big/\bar{\varphi}^{293\ \mathrm{K}}_{t\to c} = dD/dt|^{T}_{t=0}\Big/dD/dT|^{293\ \mathrm{K}}_{t=0}$$

Experimental temperature dependences of relative quantum yields of probes I–IV trans–cis isomerization in glassy polystyrene are presented in Figure 6. One can see that for probes I–III quantum yields reach the maximum value at 250–270 K, and do not change upon further temperature increase. For biradical IV the quantum yield grows in the whole studied temperature range. No photochemical experiments were carried out at temperatures higher than 333 K, since at these temperatures thermal back reaction becomes significant, which leads to large errors in kinetic measurements.

The presented experimental results show that the rate of trans–cis isomerization, as well as rotational mobility of probes I–IV rise with increasing temperature. In Figure 7a, temperature dependences of an averaged quantum yield and of an averaged amplitude of quasi-librations around *x*-axis of probe I are compared. One can observe a distinct correlation between these two values. A similar correlation exists for probes II–IV (data not shown).

At temperatures higher than 250–270 K quantum yields of probes I–III remain constant, and no correlation between rotational mobility and the rate of isomerization is present. The average quasi-libration amplitude, corresponding to the cease of quantum yield growth, is 20–25°. The quantum yield of isomerization and quasi-libration amplitude of probe IV correlate in the whole temperature range under consideration.

The existence of the maximum quantum yield for probes I–III implies that at sufficiently high temperatures the mobility is sufficient for an unhindered reaction to take place. In case of probe IV, no maximum value is observed. Besides, at 293 K the quantum yield of trans–cis isomerization of probe IV is an order of magnitude less than for probes I–III. Thus, it can be stated that isomerization of biradical IV requires higher rotational mobility, than that in required in the case of monoradicals I–III. This difference is apparently caused by the structures of the probes (Figure 1). For probes I–III, isomerization can proceed by the displacement of a small phenyl fragment of azobenzene moiety. The mobility of the molecule corresponding to the average quasi-libration amplitude of 20–25° appears to be sufficient for an unhindered phenyl rotation during an elementary act of the reaction. In case of probe IV, displacement of a significantly bigger fragment is required for the isomerization to occur. Therefore, the quantum yield continues to increase at high temperatures, and the conditions of unhindered reaction were not reached in our experiments.

In the conditions of kinetic inequivalence, only the molecules which have sufficient molecular mobility are reactive. Let us suppose that upon light irradiation a molecule can isomerize only if its quasi-libration amplitude exceeds a certain critical value, L_c. Then the fraction of molecules, which have sufficient rotational mobility, must be equal to the fraction of molecules, which isomerize after long irradiation, i.e. to the final extent of isomerization. Knowing the final reaction extent and the shape of the distribution of libration amplitudes, one can obtain the L_c value for the probe under consideration. If the model presented here is correct, and the reaction probability is determined solely by quasi-libration amplitudes, then the value of L_c for a given probe must not change with temperature.

The number of reactive molecules, measured as final cis fraction at various temperatures, is shown in Figure 3 as hatched areas. One can see that in a broad temperature range, the value of L_c remains practically the same. Similar results were obtained for other

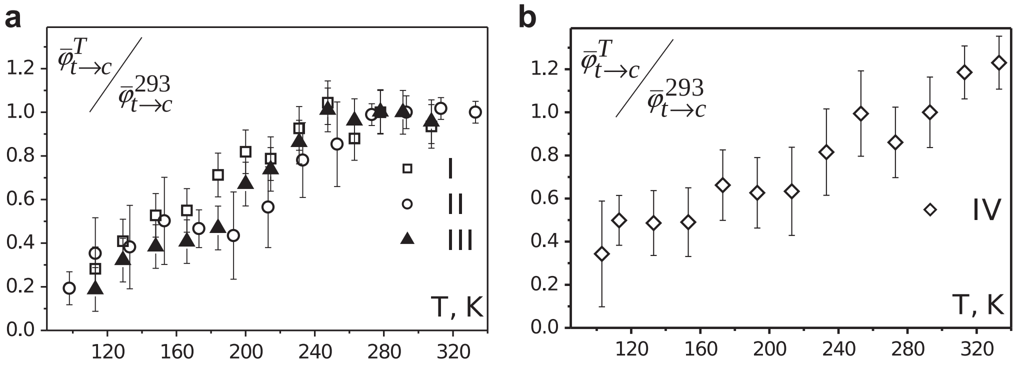

Figure 6. Temperature dependences of trans–cis isomerization quantum yields of probes I–III (a) and IV (b) in polystyrene.

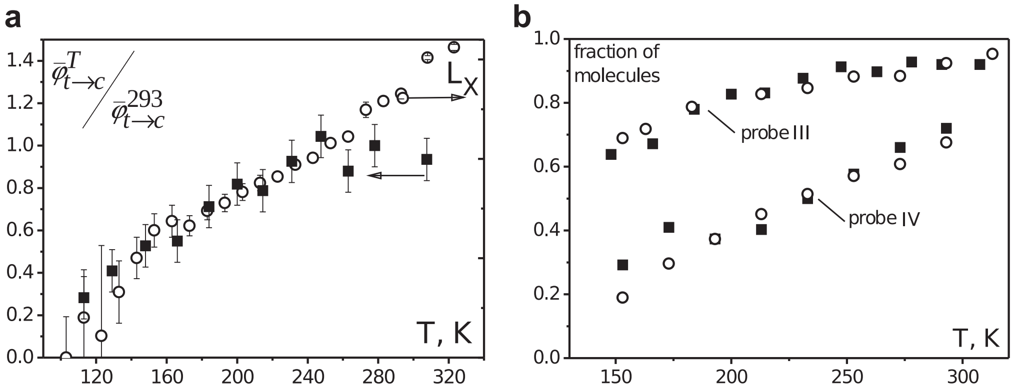

Figure 7. Relationship between rotational mobility and reactivity: (a) temperature dependences of average quantum yields (squares) and quasi-libration amplitudes (circles) of probe I in polystyrene; (b) temperature dependences of the final extent of trans–cis isomerization (squares) and fraction of molecules with quasi-libration amplitude, higher than critical (circles) for probes III and IV; the extent of trans–cis isomerization in the solution is taken equal to 1.

studied probes. Average values of critical libration amplitudes L_c for probes I–IV, were measured to be 14°, 10°, 5° and 13°, respectively. In Figure 7b, for probes III and IV temperature dependences of the final trans–cis isomerization extent and of fraction of probes with quasi-libration amplitudes larger than L_c, are compared. One can see that in the interval of 150–300 K the extent of isomerization is determined by the number of molecules with sufficient libration amplitudes. At lower temperatures the information about rotational mobility cannot be obtained with required precision due to the broadening of the ESR spectra.

In conclusion, in this work it was shown that

- molecules of a dopant dispersed in glassy polymer have a distribution of the amplitudes of high-frequency angular displacements (quasi-librations); average amplitudes of quasi-librations grow with increasing temperature;
- the distribution of molecules according to the probability of monomolecular trans–cis photoisomerization reaction exists in the glassy medium; the distribution of reaction probabilities and the distribution of molecular mobility are shown to be interrelated;
- the rate of photoisomerization shows clear correlation with the average quasi-libration amplitude;
- when the sufficient value of quasi-libration amplitude is reached, the polymer medium ceases to restrict the rate of photoisomerization.

These results indicate that in the glassy polymer medium the probability of chemical reaction is determined by whether the displacements of molecular fragments required for the reaction are possible. The elementary act of a reaction occurs if the medium allows the displacements of fragments of sufficient volume with sufficient frequency and amplitude. Measurements of quasi-libration amplitudes of spin probes can be utilized to predict the rates of chemical transformations in solid polymers.

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