Molecular Mobility of Nitroxide Spin Probes in Glassy Polymers: Models of the Complex Motion of Spin Probes

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ABSTRACT: The rotational mobility of molecules in glassy polymers was investigated by quantitative simulations of electron spin resonance spectra of nitroxide spin probes with molecules of different sizes. The motional models were determined unambiguously when the experimental and calculated spectra coincided within the level of experimental error. Temperature ranges in which different motional models were applicable were determined. Quasi-librational movements and the distribution of rotational mobility were found to be necessary for the qualitative description of spin-probe mobility in glassy polymers. The quantitative and empirical characteristics of rotational mobility were examined. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 102–110, 2011

Key words: ESR/EPR; modeling; molecular dynamics

INTRODUCTION

The spin-probe method is a powerful tool for studying molecular mobility in various media.[1–9] The method is based on an analysis of electron spin resonance (ESR) spectra of nitroxide radicals in the investigated medium. Mobility data are usually quantified by the rotational correlation time (τ_c), which corresponds to a typical time during which a molecule maintains its spatial orientation. Mobility data are obtained mostly with simple correlations of τ_c and experimental parameters of the spectrum (e.g., line amplitudes and widths and separation of outer extrema).[1–10] The apparent advantage of this correlation approach is the possibility of evaluating the characteristics of molecular mobility directly from ESR spectra. Unfortunately, in the case of glassy polymers, the data obtained with correlation formulas contradict those obtained with other methods.[11–16] This is not surprising because these formulas were developed for ESR spectra of nitroxide probes in low-molecular-weight media. More detailed and exact data can be obtained by the numerical simulation of ESR spectra and by the comparison of the calculated and experimental spectra.[12,15,17–19] However, in the case of glassy polymers, quantitative numerical simulations often fail to reproduce the experimental spectra quantitatively. Thus, information obtained by the spin-probe method for glassy polymer media remains insufficiently reliable. To overcome these difficulties, we undertook a detailed reexamination of the temperature dependences of ESR spectra of spin probes in glassy polymers in the temperature range of 77–400 K.[20]

Three nitroxides of different sizes were used as spin probes: 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (TEMPON), di-*p*-anisyl nitroxide (DPAN), and a fullerene molecule carrying a nitroxide substituent (FPO). Glassy polystyrene (PS), poly(vinyl butyral) (PVB), poly(vinyl trimethylsilane) (PVTMS), and amorphous Teflon AF-2400 were studied (Figure 1 and Table I).

Earlier, we identified three temperature ranges with distinct types of temperature dependence of ESR spectra.[20] An example of the temperature ranges for ESR spectra of TEMPON in PS is shown in Figure 2. At low temperatures (temperature range I), the spectra slowly change as the temperature increases, and they retain a slow-motion shape. Almost all ESR spectra in this temperature range can be quantitatively simulated with a quasi-libration model.[17] The term *libration* is commonly used for harmonic angular oscillations of molecules in crystals with frequencies of 10^{11}–10^{12} s^{-1} and amplitudes up to 2–3°. Quasi-librational motions are stochastic angular displacements with frequencies of 10^{10}–10^{12} s^{-1} and amplitudes up to 30–60°. This type of motion in glasses has been evidenced by high-frequency ESR,[21] magnetization transfer,[22] and spin–echo experiments.[23–26] The simulation of ESR spectra[15,17] has shown that amplitudes of quasi-librations increase and the distribution of quasi-libration
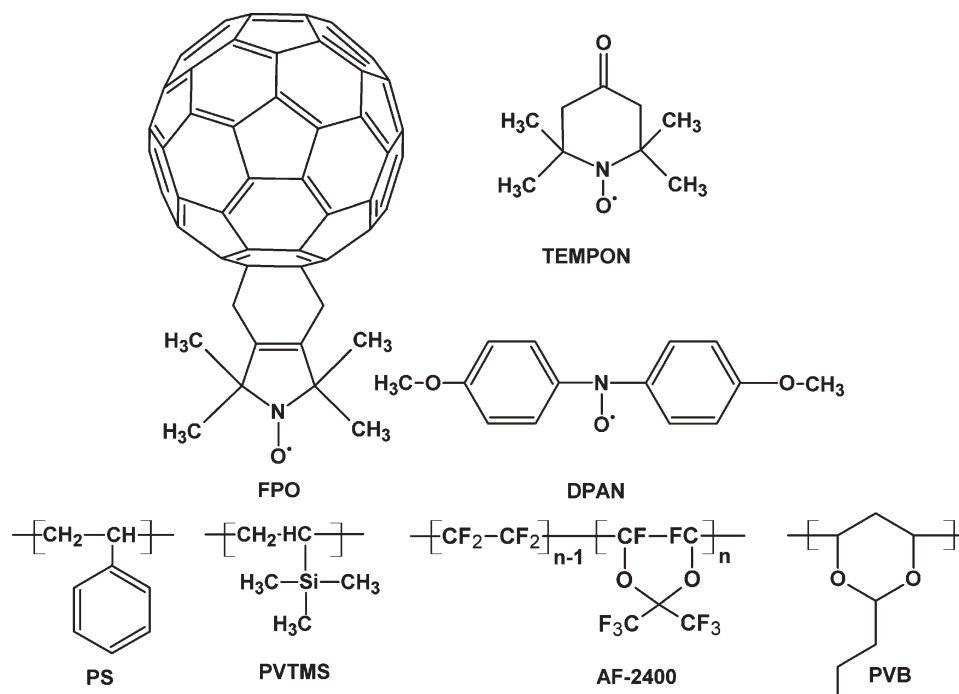
Figure 1 Structures of the nitroxide spin probes and the monomers of the investigated polymers.

amplitudes becomes apparent as the temperature rises within temperature range I.

At higher temperatures, qualitative changes in spectra are observed (temperature range II).[20] In this range, the spectrum shape typical for a slow-motion regime transforms into the shape typical for fast motions, that is, a three-component spectrum. This transformation requires 150–200 K in polymers versus 10–30 K in low-molecular-weight media.

A new phenomenon has been revealed in glassy polymers at and just below the glass-transition temperature (T_g), that is, in temperature range III.[20] Spectral lines narrow, whereas the ratios of amplitudes of different components vary insignificantly. The shape of ESR spectra in temperature ranges II and III has not been described quantitatively up to now. Calculations within frameworks of commonly used motional models (Brownian rotational diffusion, free diffusion, and micro-order/macro-disorder) fail to fit experimental spectra in a wide temperature range below the glass transition. As a rule, discrepancies between calculated and experimental ESR spectra heavily exceed experimental errors in the case of glassy polymers. The distribution of molecular mobility in glassy polymers is one of the possible causes of this failure.[27–28] The hypothesis of molecular mobility distribution is often used for the interpretation of multicomponent shapes of ESR spectra.[3,9,29–32] Nevertheless, simulations of ESR spectra with molecular mobility distributions have been performed in only a few works.[18–19,33–34] It has

been shown that some improvement of the simulation can be achieved when the distribution of molecular mobility is taken into account. Literature data, however, are insufficient for reconstructing the whole picture of molecular dynamics and motional models in glassy polymers.

Thus, the aim of this study was to obtain more reliable and detailed information on molecular mobility in glassy polymers by the simulation of ESR spectra over a wide temperature range below the glass transition. The requirement of agreement between simulated and experimental spectra within experimental error makes the method very sensitive to the choice of the motional model.

EXPERIMENTAL

The structures of the polymers and nitroxide spin probes used in this study are shown in Figure 1. Some properties of the glassy polymers are listed in Table I. Details of the sample preparation and ESR study are described in our previous paper.[20]

TABLE I
Some Properties of the Investigated Polymers

Polymer	T_g (K)	Free-volume fraction (%)[a]
AF-2400	510	32
PVTMS	423	20
PS	373	15
PVB	330	10

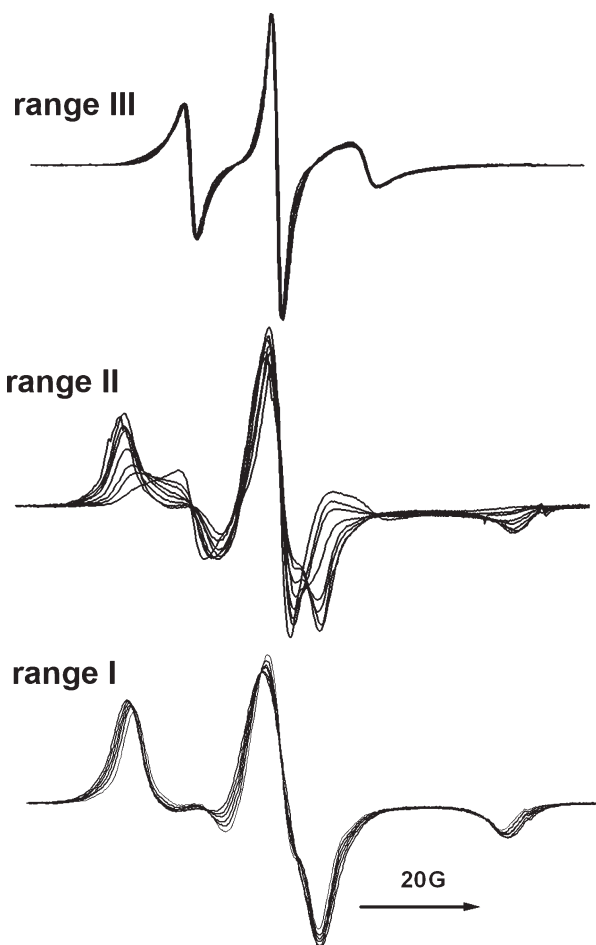[a] The data were estimated using Bondi method.[35]

Figure 2 Three temperature ranges with distinct types of temperature dependence for ESR spectra of TEMPON in PS: temperature range I (120–180 K), temperature range II (180–330 K), and temperature range III (330–404 K).

SIMULATION PROCEDURE

Simulations of ESR spectra were performed with nonlinear least-square algorithm. The discrepancy between calculated and experimental spectra (Σr_i^2, where r_i is the difference between the calculated and experimental points of a spectrum) was normalized to the spectrum area (S), which was obtained by double integration, and to the number of points (n) in the model spectrum. Parameters were varied to minimize the normalized sum of squared deviations between calculated and experimental spectra ($D = \Sigma r_i^2 / Sn$). An adaptive least-square procedure[36–37] was used for this purpose. Details of the calculation of the ESR spectra within a rigid limit and the obtained magnetic parameters of nitroxide radicals are described elsewhere.[17]

A modification of Freed's program was used in our work.[38] The original version (1.6) allows the simulation of ESR spectra in the framework of Brownian rotational diffusion, free diffusion, jump diffusion,

and micro-order/macro-disorder models. The modified program also allows the following:

1. Calculating ESR spectra under the assumption of simultaneous quasi-librations and rotation of the spin probe (for this purpose, the magnetic parameters of the spin probe were pre-averaged in accordance with a quasi-libration model;[17] then, the calculation of the ESR spectra was performed with the pre-averaged magnetic parameters in Freed's program).
2. Taking into account the lognormal distribution of correlation times:

$$\rho(R) = \begin{cases} 0, & R < 0 \\ \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(\ln R - \ln R_0)^2}{2\sigma^2}\right), & R > 0 \end{cases} \quad (1)$$

where ρ is the probability density function; R is the rotational diffusion coefficient; and $\ln R_0$ and σ are the center and dispersion of the distribution, respectively.

Because the determination of motional parameters by the simulation of ESR spectra is an inverse problem, some restrictions were imposed on the simulation results to avoid ambiguity. The description of ESR spectra was considered satisfactory when the following requirements were met:

1. Discrepancies between simulated and experimental spectra should be within experimental error. In our work, the sum of the squared deviations of a computed spectrum versus an experimental spectrum ($D = \Sigma r_i^2 / Sn$) that corresponded to this requirement was 1×10^{-5}.
2. The positions of components in simulated and experimental spectra should coincide.
3. The simulation procedure should converge to the same optimal set of resulting parameters independently of the choice of the initial parameters within physically reasonable limits.
4. The temperature dependences of the obtained motional parameters and parameters of individual line widths should be physically meaningful.

We have found that it is nearly impossible to obtain equally good satisfactory descriptions of the same experimental spectrum in the framework of two different models of molecular mobility. The exceptions are most low-temperature spectra and spectra at the highest temperatures. Thus, the two former conditions lead to a unique determination of a motional model, whereas the latter two are responsible for the unambiguity and reasonability of motional parameters.

RESULTS

ESR spectra of nitroxide radicals in glassy polymers in temperature range III consist of three components.
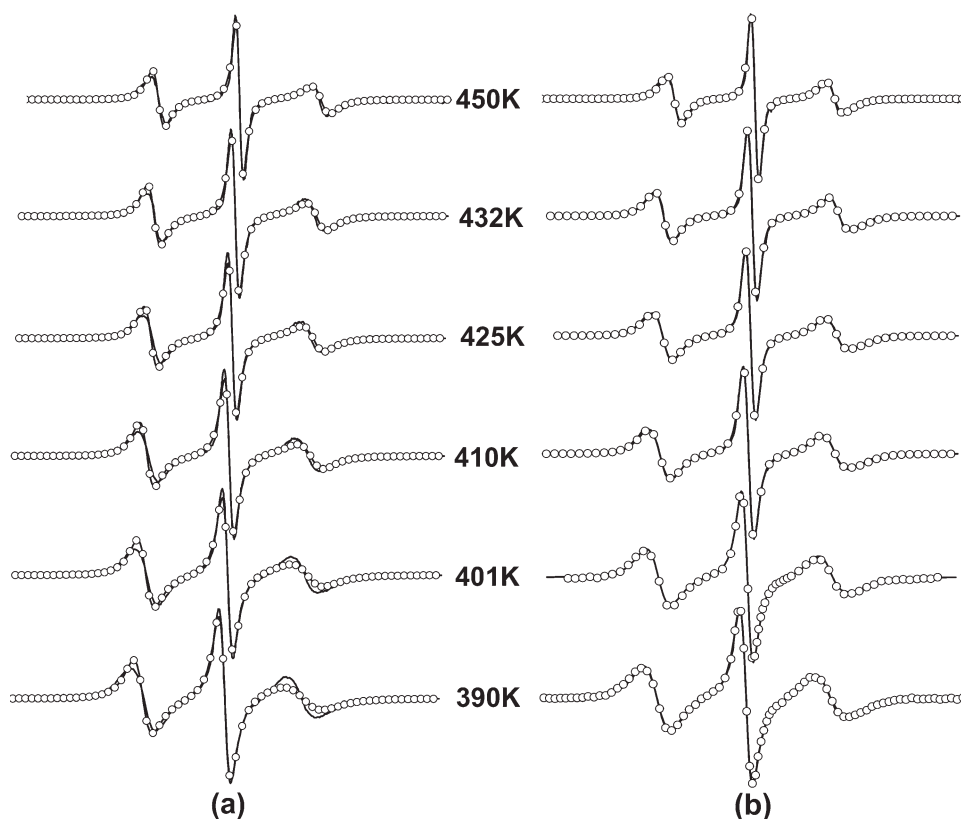
Figure 3 Spectra obtained in the framework of (a) Brownian rotational diffusion and (b) simultaneous Brownian rotational diffusion and quasi-librations for TEMPON in PVTMS. Lines are experimental spectra, and points are simulated spectra.

This type of spectrum is considered motionally narrowed. Usually, such spectra are described in the framework of a Brownian rotational diffusion or jump model. However, ratios of component amplitudes, nearly independent of temperature, are poorly reproduced by any of these models. The results of the simulation of ESR spectra of TEMPON in PVTMS with a Brownian diffusion model are shown in Figure 3(a) as an example. The agreement between the simulated and experimental spectra at 450 K is satisfactory. However, the agreement becomes worse and the amplitude ratios change as the temperature decreases. Similar results were obtained for the temperature dependence of the ESR spectra in all studied polymers.

As shown earlier, the motion of nitroxide radicals in glassy polymer matrices at low temperatures is highly restricted. Experimental spectra in the corresponding temperature range are satisfactorily described by a quasi-librational model.[15,17] Apparently, the motion of a probe is restricted by the cage walls. As the temperature becomes higher, the mobility of the polymer fragments forming the cage increases, and the cage starts to rearrange and re-orient. Thus, it is possible to suggest that the probe participates in two types of motion: fast quasi-librations restricted by the cage and slow Brownian dif-fusion caused by the cage rearrangement. The results of the simulation of ESR spectra for TEM-PON in PVTMS in the framework of this combined model are shown in Figure 3(b). A satisfactory description is observed in the temperature range of 450–350 K. Similar results were obtained for TEMPON in PS and AF-2400.

The full set of anisotropic motional parameters cannot be determined precisely from X-band (3-cm wavelength) ESR spectra because of the limited reso-lution of the spectra. Some assumptions of motional anisotropy are required to avoid ambiguity in the obtained results. We have found that the assumption of anisotropic quasi-librational motions caused by the anisotropic shape of the cage and the isotropic reorientation of the cage leads to the most appropri-ate approximation. The values of quasi-libration amplitudes of nitroxide motion in this temperature range are as high as 50–70°. The τ_c values of Brown-ian rotational diffusion in these simulations are within $10^{-8} - 10^{-9}$ s.

Experimental spectra in the middle temperature range (range II) are the most difficult to fit because their shape is complex and significantly depends on the temperature. On the one hand, the model of simultaneous quasi-librations and rotation of spin probes is appropriate at higher temperatures. On the
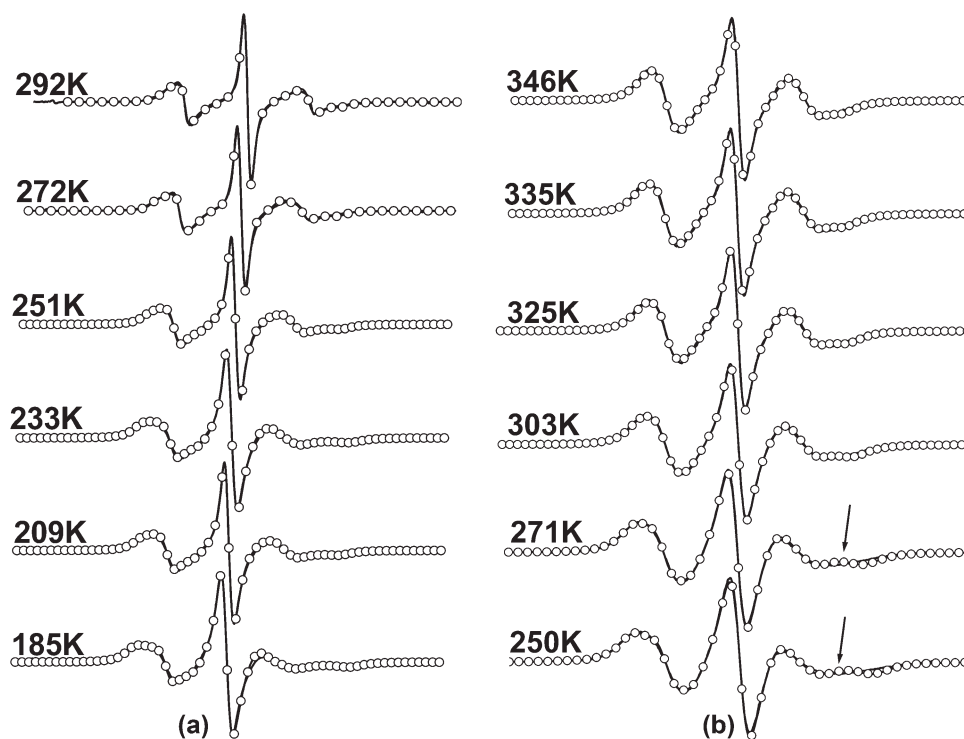
Figure 4 ESR spectra of TEMPON in (a) AF-2400 and (b) PVTMS in temperature range II. Lines are experimental spectra, and points are simulated spectra.

other hand, the distribution of quasi-libration amplitudes is observed at lower temperatures. Thus, the model of simultaneous quasi-librations and Brownian rotational diffusion with distributed correlation times seems to be the most reasonable motional model for temperature range II. A lognormal distribution of the correlation times was used as a model distribution. Indeed, a satisfactory agreement between calculated and experimental spectra in temperature range II was obtained with this model (Fig. 4). Taking into account quasi-librations is a necessary requirement for a satisfactory description of these spectra.

Some slight differences (marked with arrows in Fig. 4) between simulated and experimental spectra may be caused by an imperfection in the lognormal distribution. We used the lognormal distribution for the following reasons. The Gauss distribution has been shown to be a good description of the free-volume distribution in some polymers, including PS.[39] The lognormal distribution also appears if the molecular motion occurs via activated jumps over normally distributed energy barriers.[18] The characteristic widths of the distributions obtained as a result of our simulations of spectra were found to be in the range of 0.6–1.0 decades. The obtained data conform to the literature data on the width of the distribution of correlation times in polymers.[18–19,33–34] The distribution narrows as the tem-

perature rises. Our calculations show that a distribution with a width of 0.4 decades or less does not influence the simulated ESR spectra. The results of the quantitative simulation of ESR spectra in the whole temperature range below the glass transition are presented in Figure 5 as an example. Figure 5 shows the low-temperature spectra described with the quasi-libration model.[17]

The integrated picture of the molecular dynamics of nitroxides in glassy polymers, obtained from simulations of the whole temperature dependences of ESR spectra below the glass transition, is as follows. At low temperatures, the mobility of a spin probe in a glassy polymer is highly restricted. Nitroxide molecules undergo librations and quasi-librations. As the temperature rises, quasi-libration amplitudes increase, and the distribution of molecular mobility becomes apparent in the spectra. With a further temperature increase, polymer cage rearrangements with sufficiently high frequencies begin, and Brownian rotational diffusion with distributed correlation times becomes apparent in ESR spectra concurrently with quasi-librations. The width of the distributions decreases with the temperature increasing, and spectra at the highest temperatures are satisfactorily described under the assumption of simultaneous rotational and librational motions without any distributions. Application ranges for different motional models for the simulation of ESR spectra are shown
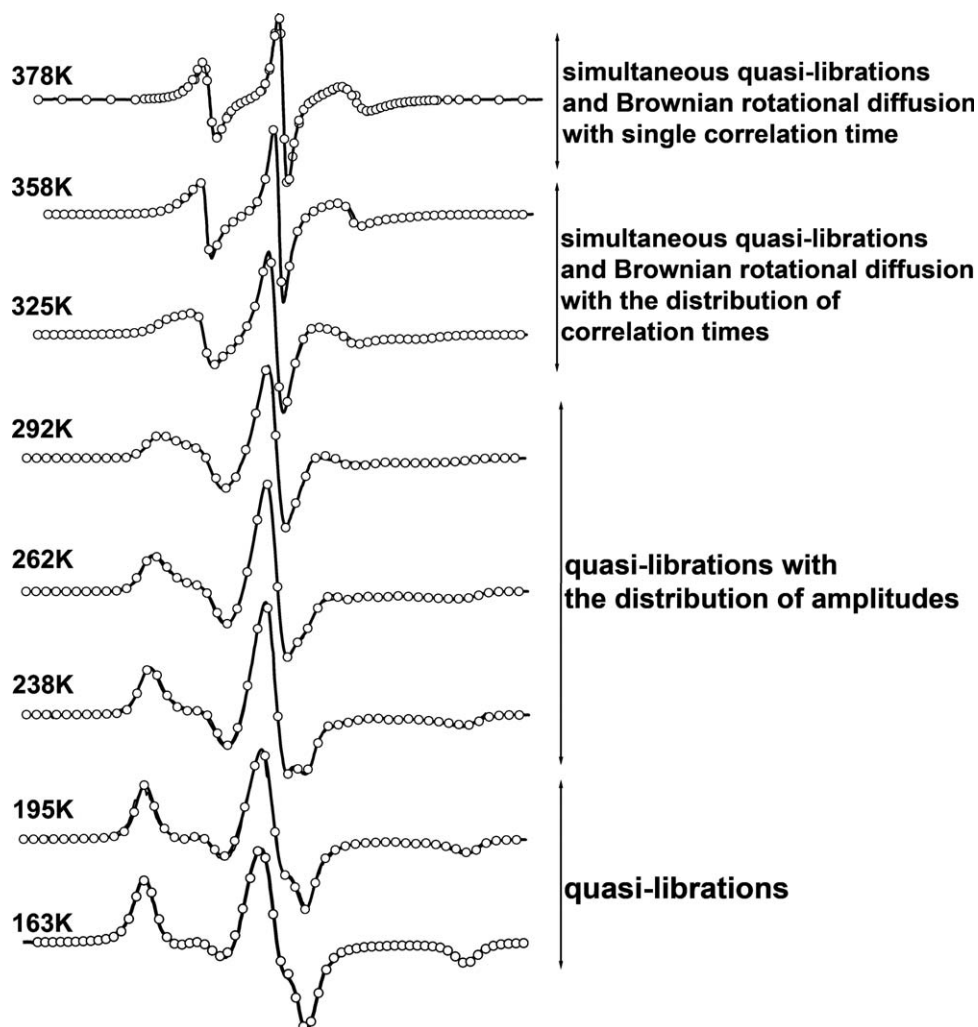
Figure 5 Results of the simulation of spectra for TEMPON in PS over the whole temperature range below the glass-transition point. Lines are experimental spectra, and points are simulated spectra.

in Figure 6. The greater the size is of the probe molecule, the higher the shift is of the applicable ranges to higher temperatures.

Unfortunately, some spectra cannot be described within experimental error with any of the motional models mentioned previously. This may be a result
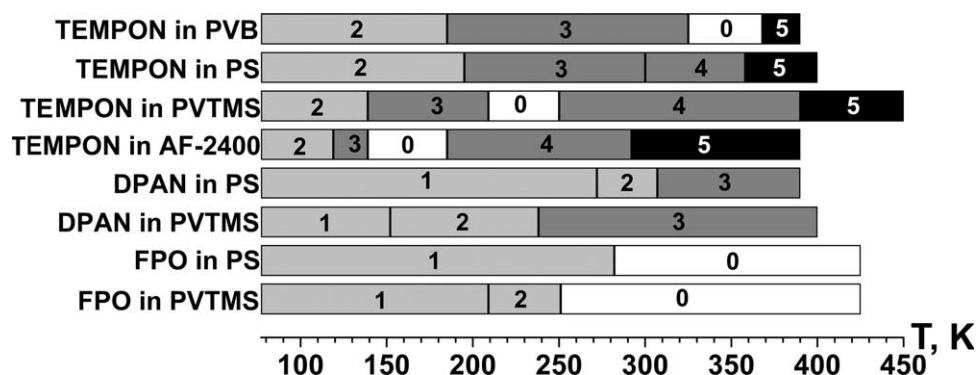

Figure 6 Temperature ranges of motional models applicable to the simulation of ESR spectra of glassy polymers: (0) the model is not defined, (1) there is a rigid limit, (2) there are quasi-librations, (3) there are quasi-librations with the distribution of amplitudes, (4) there are simultaneous quasi-librations and Brownian rotational diffusion with the distribution of correlation times, and (5) there are simultaneous quasi-librations and Brownian rotational diffusion with a single correlation time.

of the more complicated distributions of molecular mobility in real polymers. As shown in Figure 6, ESR spectra of FPO in a wide temperature range were not simulated satisfactorily. The mobility of the nitroxide moiety in this case seems to be similar to the mobility of a spin label attached to the cage wall. We have not found an appropriate motional model or distribution shape for this case.

DISCUSSION

The aforementioned simulations of spectra show that the probe mobility in a glassy polymer matrix cannot be characterized by a single value of τ_c. To obtain a quantitative agreement between calculated and experimental spectra, the slow Brownian rotational rearrangement of the polymer cage and intracage high-frequency quasi-librations should be taken into account. It seems useful to compare the characteristics of rotation mobility obtained in the course of spectral simulation and calculated with commonly used formulas for τ_c. The formulas are based on the following expression of the line width of the components $[\delta(m)]$:[1,2,5]

$$\delta(m) = (A + Bm + Cm^2)\tau_c + X \qquad (2)$$

where m is the nuclear spin projection; A, B, and C are constants depending on the magnetic parameters of the spin probe; and X is the residual line width.

The equation for the calculation of τ_c from experimental spectra based on eq. (2) is as follows:

$$\tau_c = K_{m_1 m_2}\Delta H(m_2)[(I(m_2)/I(m_1))^{1/2} - 1] \qquad (3)$$

where $I(m_1)$ and $I(m_2)$ are the amplitudes of the corresponding lines of the ESR spectrum, $\Delta H(m_2)$ is the peak-to-peak width of the component with a nuclear spin projection of $m = m_2$, and $K_{m_1 m_2}$ is a constant determined from the components of the **g** and **A** tensors.[3,10]

In accordance with eq. (3), τ_c can be calculated from the amplitudes and widths of different combinations of the three spectrum components. The results of these calculations are presented in Figure 7 and are compared with the τ_c values of cage rearrangement determined in the course of spectral simulation. When a τ_c distribution is necessary for the simulation of experimental spectra, the correlation times, averaged in accordance with the distribution, are presented.

Figure 7 shows that the values of the correlation times calculated with different combinations of spectral components are significantly less than the values obtained in the course of simulation. The nonlinearity of the Arrhenius plot, a difference in τ_c values as
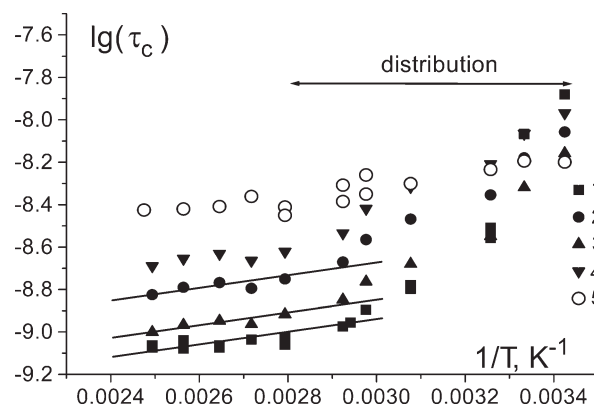

Figure 7 Arrhenius plot of τ_c values obtained (1–4) with formulas for different components of the spectra of TEMPON in PS and (5) by numerical simulation of the spectra (T = temperature).

high as 2–3-fold, and unrealistic values of constants A and B in eq. (2) are observed when τ_c is calculated with the formulas. Thus, the formulas are not reliable in the case of glassy polymers. Nevertheless, apparent activation energies calculated for TEMPON in PS and AF-2400 near T_g with formulas and spectral simulations are in approximate agreement. The obtained values are 5.3 and 8.6 kJ/mol for PS and AF-2400, respectively. A considerable difference in the values of τ_c is also observed in the low-temperature range. Similar results have been obtained for other studied polymers.

Intracage motions are successfully described by high-frequency quasi-librations. It was shown earlier that the quasi-libration amplitudes around the molecular y axis of nitroxide are the most informative values.[17] If the results of the determination of mobility parameters point to molecular distributions, averaged values can be used. The temperature dependence of the quasi-libration amplitudes around the y axis (L_y) is presented in Figure 8. The figure shows that amplitudes obtained for all temperature ranges produce a unified temperature dependence. Higher amplitudes are observed in polymers with higher free volumes. Similar results have been obtained for the dependence of quasi-libration amplitudes on the probe size: the lower the molecular volume is of the probe, the higher the amplitudes are. This observation is in accordance with data published earlier.[5–6,40–41] Violations of the smoothness of high-temperature parts of the dependence in Figure 8 (e.g., dependence 1) show that the division of mobility into quasi-librations and Brownian rotations becomes unreliable when the amplitudes of librations achieve high values.

The results of the simulation show that the molecular dynamics of spin probes in glassy polymers should be characterized by the set or spectrum of molecular movements with different amplitudes and
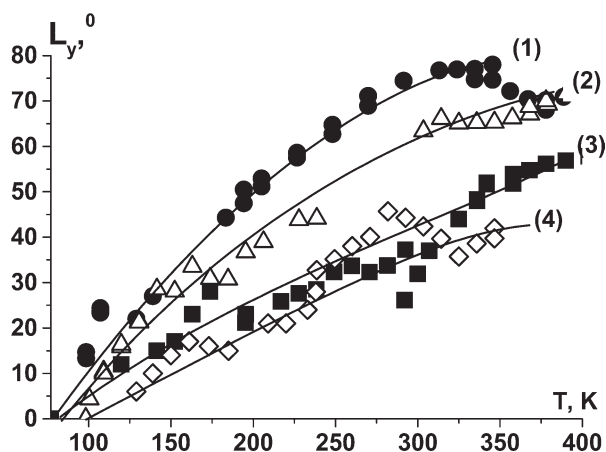
Figure 8 Quasi-libration amplitudes of TEMPON in (1) AF2400, (2) PVTMS, (3) PVB, and (4) PS.

frequencies. A unified model describing molecular mobility in polymers over the whole temperature range seems to be rather complicated. Molecular mobility in glassy polymers can be illustrated qualitatively by relaxation curves (Fig. 9). The ordinate axis characterizes the time required for the rotational displacement or deviation of a molecule from the original position by the angle specified on the abscissa axis. The shape of the ESR spectrum depends on motions with frequencies and amplitudes defined by the window of sensitivity. The sensitivity window for X-band ESR spectroscopy is shown in Figure 9. The window is shifted to higher frequencies when high-frequency ESR spectroscopy is used. The gray area corresponds to high-frequency movements resulting in partial averaging of magnetic parameters of probes. These movements manifest themselves in ESR spectra as quasi-librations. Movements with amplitudes exceeding 90° are apparently observed as rotations. If a considerable part of the
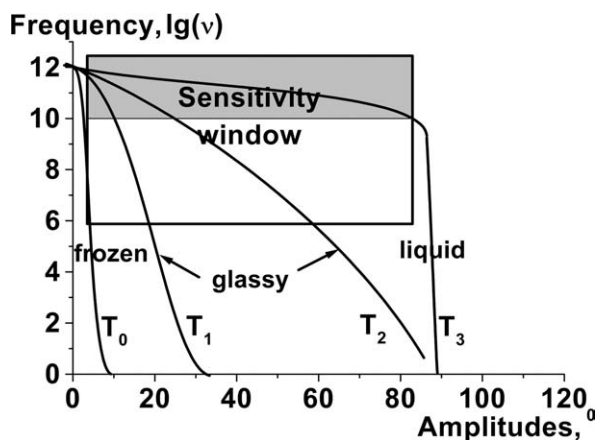
relaxation curve falls in the white area of the sensitivity window, the distribution of molecular mobility should be taken into account for satisfactory agreement between simulated and experimental ESR spectra. Curves typical of glassy and liquid states are also shown in the figure.

A full numerical description of molecular dynamics involves amplitudes of quasi-librational motions, correlation times of Brownian diffusion, shapes of distributions of quasi-libration amplitudes, and correlation times. These data can be obtained by the simulation of ESR spectra. However, simulation are too complicated procedure to run whenever the dynamics of two polymers are being compared. The amplitude-to-area factor (K_f) suggested earlier[20] is simpler to use. It is defined as the ratio of the amplitude of the central spectral component to the area under the spectrum. K_f is a dimensional quantity ($1/G^2$ in our work) independent of the spectrum amplitude and some conditions of ESR spectrum registration. Because K_f is a measure of spectrum narrowing, it can be used as an empirical characteristic of molecular mobility. An analysis of the K_f value leads to the same qualitative conclusions on the molecular dynamics of nitroxide in glassy polymers as the quantitative simulation of ESR spectra. For example, the temperature dependence of K_f for TEMPON in different polymers is shown in Figure 10. K_f values for TEMPON below 120 K are similar in different polymers. At higher temperatures, K_f in AF-2400 is greater than K_f in PS, and the latter is greater than K_f in PVB. Therefore, the molecular mobility of TEMPON at these temperatures in polymers decreases as follows: AF-2400 > PS > PVB. This sequence correlates with the free-volume fraction in the polymers (see Table I). This conclusion conforms to the temperature dependences of quasi-libration amplitudes in Figure 8 and the temperature ranges of motional models in Figure 6.
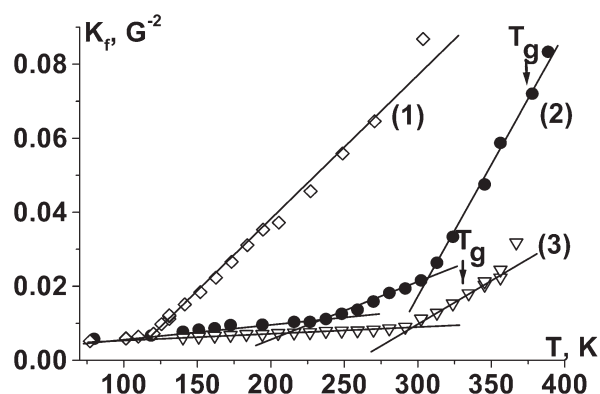

Figure 9 Relaxation curves typical for different states of matter. The curves are schematically presented for different temperatures with the following relationship: $T_0 < T_1 < T_2 < T_3$.

Figure 10 Temperature (T) dependence of K_f for TEMPON in (1) AF-2400, (2) PS, and (3) PVB.

CONCLUSIONS

The aforementioned results demonstrate that the rotational molecular mobility of spin probes in glassy polymers is the set of molecular movements with different amplitudes and frequencies. The following factors characterize molecular mobility: the amplitudes of quasi-librational motion, the correlation times of Brownian diffusion, and the shape of the distribution of quasi-libration amplitudes and correlation times. These data can be obtained by the simulation of ESR spectra. The temperature ranges for the applicability of different motional models for the simulation of ESR spectra have been determined. Fast quasi-librational movements and the distribution of rotation mobility should be taken into account for qualitative descriptions of ESR spectra of nitroxides in glassy polymers. K_f is proposed as an easily calculated empirical characteristic for the comparison of molecular mobility in different polymers.

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