

High-field electron paramagnetic resonance in polymers and glasses: criteria for the optimal choice of the spin probe

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The reorientation of guest paramagnetic molecules free radicals spin probes in the host polymers and glass formers is studied by High-Field High-Frequency Paramagnetic Resonance (HF²EPR) spectroscopy at three different Larmour frequencies, 95, 190 and 285 GHz. The structural change of the host that occurs close to glass transition temperature changes the reorientation regime of the molecular spin probe. For the slow tumbling regime of the rotational motion, the line shape exhibits larger sensitivity of the free radicals spin probe to both the static and the dynamics of the environment. Change of the reorientation rate lead to considerable line shifts, whereas broadening effects are not dominant. Discussion is focused on the suitable choice of the spin probe used in the HF²EPR spectroscopy in the study of the polymeric and glass formers systems.

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1. Introduction

The studies of the viscosity increase when a supercooled liquid is cooled down to the glass transition temperature and the glassy solid dynamics are very active ones [1,2,3]. Many theoretical concepts have been proposed to explain the slowing down of the dynamics close to glass transition, among these free-volume [4,5] and thermodynamic [6,7] theories. A new approach is based on the cage dynamics [8]. On approaching the glass transition, the large-scale motion becomes more and more hindered by the increasing structural constrains [1,9]. Molecules, or subunits of macromolecules, are surrounded and trapped by rigid pockets, which are usually referred to as cages. The cage concept is rather intuitive and fruitful in that it may be incorporated in formal theoretical treatments like the mode-coupling theory [10] and recent extensions to deal with polymer chains [11]. For the study of glassy solid dynamics, particular interest and current strong controversy is the so called fast dynamics of glasses, occurring in the time window 1-10² ps with several studies carried out mainly by neutron [12,13,14] and Raman scattering [15,16,17]. It is observed that on heating in a temperature range below T_g the dynamics of glass forming systems deviates from the harmonic behaviour and quasideelastic scattering starts to accumulate in the low frequency range of the scattering function S(Q,ω). Accordingly, the temperature dependence of the atomic mean square displacement also starts to deviate from the linear dependence.

Electron paramagnetic resonance (EPR) spectroscopy is a method for characterizing structure, dynamics, and spatial distribution of paramagnetic species. Diamagnetic

materials can be studied by using spin probes, which are stable paramagnetic species such as nitroxide radicals and transition metal ions. Nitroxide radicals are primarily used to probe soft condensed matter, while transition metal or rare earth ions are also popular as spin probes in inorganic optical glasses. The question of whether relaxation times measured by probe methods tend to be as tractable as bulk measurements can be answered with reference to results of the groups of Sillescu [18], of Ediger [19], of Richert [20,21] and of Leporini [22,23].

The HF²EPR spectrum of a spin label is sensitive to rotational motions with correlation times in the 10⁻¹²-10⁻⁷ s ranges. For the slow tumbling regime it has recently been proved that contrary the usual belief, on increasing the Larmour frequency, the HF²EPR line shape exhibits larger sensitivity to the rotational motion of the radicals. Changes of the reorientational rate lead to considerable line shifts, whereas broadening effects are not dominant [24].

In the present paper we present a detailed temperature study of the reorientation of molecules spin probes (TEMPO, Androstane, Nonadecane) in polymers and glass former (see Fig. 1 (right)) by HF²EPR at three different Larmour frequencies (95, 190 and 285 GHz). The study demonstrates the essential role that the choice of suitable guest molecules (spin probe) has in the study of the soft condensed matter.

The paper is organized as follows. In section 2 the background on HF²EPR is presented. In section 3 experimental details are given. Results and discussions are presented in section 4. The conclusions are summarized in section 5.

2. EPR background

The EPR signal is detected in paramagnetic systems. Since most polymers and glass former are diamagnetic, paramagnetic probe molecules (spin probes) are usually dissolved in them. The main broadening mechanism of the EPR line shape of the spin probe is determined by the coupling between the reorientation of the latter and the relaxation of the electron magnetization \mathbf{M} via the anisotropy of the Zeeman and the hyperfine magnetic interactions. When the molecule rotates, the coupling gives rise to fluctuating magnetic fields acting on the spin system. The resulting phase shifts and transitions relax the magnetization and, in turn, broaden and shift the different lines contributing to the pattern of the EPR line shape [25].

Fig. 1 (left) illustrates the different patterns of an EPR spectra for a nitroxide dissolved in a diamagnetic host. From top to bottom the EPR line shape change from a very fast reorientation to a slow tumbling motion. For reorientation that is much faster than the EPR time scale the anisotropy of interactions is averaged, and a triplet of fairly narrow lines is observed. The splitting is due to the hyperfine coupling to the ^{14}N nucleus and the widths of the three lines due to the hyperfine dependent relaxation rates (fast limit regime). For slower reorientation this line width differences become more pronounced, and the clearly discernible triplet structure is lost (transition to slow tumbling regime). When the reorientation rate decreases further, the spectrum becomes significantly broader, as the anisotropy of g and hyperfine tensors is no longer averaged (slow tumbling regime). In this regime the line shape is most sensitive to the rate and specifics of the reorientation process. And in this respect an elementary tool to appreciate the sensitivity of the line shape to the rotational dynamics is the distance between the outermost peaks of the line shape ΔB (see [24,25] for further details). When the reorientation rate of the spin probes decreases, the anisotropy of the Zeeman and hyperfine tensors is less and less averaged and the spectrum becomes significantly broader, i.e. ΔB increases. Finally, when the motion becomes significantly slower than the time scale of the EPR experiment, the line shape can be hardly distinguished from the line shape in the rigid limit (rigid regime).

A general property of the spin probe dissolved in disordered systems is the libration motion [26,27]. From the EPR spectra it is possible to obtain the motion parameter, i.e., the correlation time τ_c and the mean square value of the reorientation angle $\langle\Delta\theta^2\rangle$. In the last several years study of the cage dynamics by magnetic resonance spectroscopy were reported [28,29,30]. The molecular libration changes the partially averaged principal values of the hyperfine interaction and g -factor tensors and then the quantity ΔB [31], and the width of the EPR line shape. The $\langle\Delta\theta^2\rangle$ temperature dependence is consistent with the temperature dependence of the mean square displacement of molecules observed for organic glasses using Mössbauer spectroscopy[32], and neutron scattering [33].

3. Experimental details

The polymers: polybutadiene (**PB**) ($T_g=180\text{K}$, $M_w=200\text{Kg mol}^{-1}$) and polystyrene (**PS**) ($T_g=367\text{K}$, $M_w=230\text{Kg mol}^{-1}$), the glass former ortho-terphenyl (**OTP**) ($T_g=243\text{K}$, $M_w=100\text{Kg mol}^{-1}$) and the nitroxide free radicals used as spin probes: 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**) ($M_w=156.2\text{g mol}^{-1}$), 17 β -Hydroxy-4',4'-dimethylspiro(5a-**Androstane**-3,2'-oxazolidin)-3'-yloxy ($M_w=377.56\text{g mol}^{-1}$), 10-doxyl-**Nonadecane** ($M_w=368.63\text{g mol}^{-1}$) were all obtained from Aldrich and used as received. A detailed chemical structure of the spin probes used are presented in figure 1.(right) The sample was prepared by the solution method [34] by dissolving the nitroxide spin probe and the polymer in chloroform. The solution was transferred onto the surface of a glass slide and heated at $T_g+10\text{K}$ for 24 h. For the glass former the sample was prepared at temperature higher than the melting point ($T_m=333\text{K}$). The measurement was carried out in the super-cooled state of the glass former. After this procedure no chloroform was detected by NMR. The sample of about 0.8cm^3 was placed in a Teflon sample holder in a single-pass probe cell. The spin probe was less than 0.08% in weight, thus resulting in an extremely limited influence on host material.

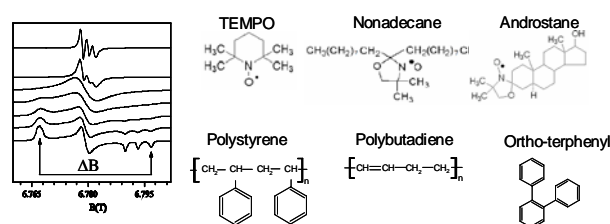


Fig. 1. Left: calculated EPR line shape at 190 GHz of a nitroxide spin probe. From top to bottom the correlation time is: $8.33 \times 10^{-11}\text{s}$, $1.5 \times 10^{-10}\text{s}$, $8.3 \times 10^{-10}\text{s}$, $1.66 \times 10^{-9}\text{s}$, $2.91 \times 10^{-9}\text{s}$, $4.58 \times 10^{-9}\text{s}$, $1.0 \times 10^{-8}\text{s}$. Right: chemical structure of the spin probes TEMPO, Nonadecane, Androstane and of guest matrix PS, PB, OTP.

Appreciable broadening of the HF^2EPR line shape due to the spin-spin interaction is observed for concentrations larger than 0.2% in weight. No segregation of the spin probe was evidenced in none of the samples. The EPR experiments were carried out on the ultrawide-band HF^2EPR spectrometer which is detailed elsewhere [35].

4. Results and discussion

Fig. 2 shows the experimental HF^2EPR line shape at 95 GHz and 285 GHz of spin probe TEMPO in PS. Even if the temperature range is much below the PS glass transition temperature, the reorientation rates of the spin probe is still changing the HF^2EPR line shape feature. At temperatures above 270 K ($T_g=97\text{K}$), the spin probe reorientation rate is too fast and the Zeeman and hyperfine

interactions are averaged. For temperature below 270 K the slow tumbling regime motion of the spin probe occurs and a careful line shape analysis was reported in ref. [24,36,37,38]. One can remark that below about 270 K the pattern of the HF²EPR line shape is virtually frequency independent. This allows the joint study of the ΔB parameter for the different frequencies.

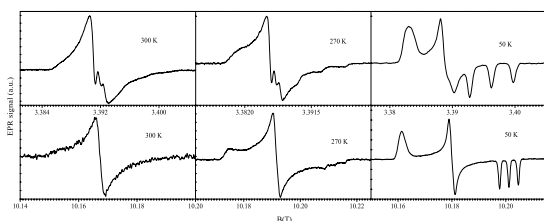


Fig. 2. Comparison between the experimental HF²EPR line shape at 95 GHz (top) and 285 GHz (bottom) of TEMPO in PS in temperature range between 50 K and 300 K.

Fig. 3 shows the temperature dependence of the distance ΔB and the average line width at 95 GHz, 190 GHz and 285 GHz of spin probe TEMPO in PS. The evidence that ΔB is still changing at temperature as low as 50 K proves that the reorientation motion of TEMPO is detectable even at such low temperatures. It can be seen that the width approaches a plateau value below 200 K signalling less sensitivity to the TEMPO reorientation than the quantity ΔB , which is a measure of the position of the lines. Noticeably, the reorientation dynamics affects the position of the lines contributing to the pattern of the HF²EPR line shape, more than their width.

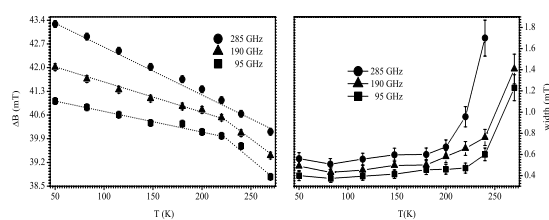


Fig. 3. Left: temperature dependence of the quantity ΔB of TEMPO in PS at 95GHz, 190 GHz, 285 GHz. Dashed line: guide for the eye. Right: Average line width of the three (190 GHz and 285 GHz), and two (95 GHz) high-field outermost peaks of the line shape.

Fig. 4 shows the experimental HF²EPR line shapes of two different spin probes in the supercooled OTP glass former at 95 GHz and 285 GHz at temperatures above the OTP glass transition temperature ($T_g=243K$). The first tentative to study the supercooled state of OTP was using the spin probe TEMPO. As one can see from Fig. 4 the spin probe motion of TEMPO is fast at both frequencies and the line shape partially averaged. In this regime the information of the spin probe dynamics is retrieved only by using accurate numerical simulation of the whole EPR spectrum.

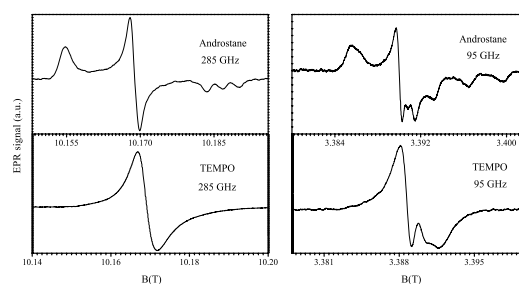


Fig. 4. Experimental HF²EPR line shapes of different spin probes in the OTP glass former at 293 K.

In order to obtain the slow tumbling regime for the HF²EPR line shape pattern, in which ΔB can be defined, the Androstane spin probe is more suitable. Due to its large size in fact the Androstane spin probe motion undergoes slow rotational dynamics resulting in a clear definition of the peaks needed to measure ΔB . Whereas in the same temperature range the dynamics of the smaller spin probe TEMPO is too fast to define ΔB . A full discussion of this temperature dependence is beyond the purpose of the present note and will be presented elsewhere.

Fig. 5 shows the temperature dependence of the experimental HF²EPR line shape of spin probe

TEMPO at 285 GHz and of spin probe Nonadecane at 95 GHz dissolved in PB and the respective ΔB temperature dependence. The temperature range of interest is around the PB glass transition temperature, $T_g-30 K < T < T_g+50 K$. As one can see from Fig. 5 the HF²EPR line shape of spin probe Nonadecane dissolved in PB in the all temperature range has the slow tumbling regime pattern. However, a close inspection of the experimental line shape and ΔB temperature dependence shows that the line shape is not changing. This means that the spin probe dynamics is too slow to be investigated by the HF²EPR, i.e., the line shape is in the rigid regime.

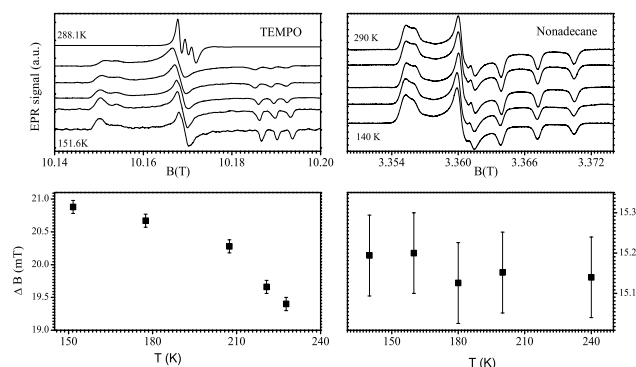


Fig. 5. Top: temperature dependence of experimental HF²EPR line shape at 285 GHz of TEMPO (left) and at 95 GHz of Nonadecane (right) in PB. Bottom: temperature dependence of quantity ΔB for TEMPO (left) and Nonadecane (right) in PB (see Fig. 1 for details).

The problem is solved by changing the spin probe Nonadecane with the smaller spin probe TEMPO. For temperature above 228 K, the spin probe TEMPO is moving fast, the Zeeman and hyperfine interactions are averaged and the quantity ΔB is not defined. Nevertheless, below 228K, the slow tumbling HF²EPR line shape pattern is obtained. As one can see from Fig. 5 in the temperature range of interest a variation of about 1.5 mT of quantity ΔB is observed. A full discussion of this temperature dependence is beyond the purpose of the present note and will be presented elsewhere.

5. Conclusions

The reorientation of different paramagnetic molecules below and above the glass transition temperature of different polymers and glass former is studied by HF²EPR spectroscopy at three different frequencies. Contrary to the usual belief, increasing the Larmor frequency leads to a remarkable line shape sensitivity to the rotational motion of radical. The numerical calculation that are usually performed to get information on the spin probe dynamics are largely simplified in the slow motion regime where details on the cage dynamics can be extracted from the experimental data by measuring the line shift ΔB . This determines the optimal choice of the spin probe. The direct connection between the mean square value, $\langle \Delta\theta^2 \rangle$, of the reorientation angle and the quantity ΔB , could reveal important information on molecular dynamics in glassy media and high viscosity systems.

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